Open quantum systems at finite temperature

Jean Richerta * and Tarek Khalilb †

a Institut de Physique, Université de Strasbourg, 3, rue de l’Université, 67084 Strasbourg Cedex, France
b Department of Physics, Faculty of Sciences(V), Lebanese University, Nabatieh, Lebanon

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Abstract

The consistent definition of the thermodynamic functions of small open quantum systems in contact with an environment in equilibrium with a heat bath has been the subject of many debates in the quantum community. In the present work we reproduce and comment parts of a recent approach of this subject by Rivas [15]. This approach overcomes the controversial discussions generated by the coupling between a system and its environment for any type of coupling between the two parts and allows for a consistent description of the thermodynamical properties of the system strongly interacting with the bath.

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1 Introduction

Quantum systems are generally never completely isolated but interact with an environment with which they may exchange energy and other physical observable quantities. Their properties are naturally affected by their coupling to the external world. The understanding and control of the influence of an environment on a given physical system is of crucial importance in different fields of

* E-mail address: j.mc.richert@gmail.com
† E-mail address: tkhalil@ul.edu.lb
physics and in technological applications and led to a large amount of investigations, see f.i. [1, 2, 3, 4, 5].

Under realistic physical conditions the environment will generally show the properties of a microscopically complex system. If at the time at which the evolution of the system is observed the environment is stationary, i.e. in thermodynamic equilibrium at a fixed temperature $T$, it is sensible to describe it in the framework of a quantum canonical ensemble if the number of particles it contains is fixed. This is the situation we consider in the present case.

In previous studies [6, 7, 8] we defined criteria which allow to classify open quantum systems with respect to their behaviour in the presence of an environment at zero temperature. In order to do so we used a general formulation which relies on the examination of the properties of the density operator of the system and its environment. The dynamical behaviour of this operator is governed by the structure of the Hamiltonians of the system, its environment and the coupling Hamiltonian which acts between them. The time-dependent density operator is a crucial quantity in the present context. We work it out for the case where the system is at the temperature of its environment, i.e. staying at thermodynamical equilibrium when evolving in time.

The introduction of a system in contact with an environment at finite temperature puts the system into a thermodynamical framework. Hence it is described in terms of thermodynamical functions and the description must be consistent with the laws of thermodynamics, in particular the second one concerning the entropy. This situation is due to the coupling of the system to an external environment. This coupling generates an ambiguity concerning the definition of the system, hence a problem with the determination of the thermodynamic functions and consequently with the rigorous respect of the thermodynamic laws [9, 10, 11, 12, 13, 14].

It is the aim of the present dissertation to present and to insist on some concepts which enter the recent work of Á. Rivas [15] leading to a rigorous solution of the problem.

The content of the presentation which relies partly on previous work [16] is the following. In section 2 we define the system and the environment to which it is coupled at temperature $T = 0$ and $T > 0$ as well as the expression of the density matrix which governs the evolution of the system and its environment. In the sequel we shall consider that both the system $S$ and its environment $E$ are the same finite temperature. Section 3 is the central part of the work where we define first the internal energy in $S$ and the characteristic thermodynamic functions characterizing a stationary system $S$ in equilibrium at the same temperature as $E$, then the same quantities for a system evolving in time, finally the asymptotic behaviour when time goes to infinity as well as the relative entropy evolution which verifies the expected thermodynamical behaviour predicted by the second law. In section 4 we present the expression of the time dependent density matrix which operates in $S$ space and develop some cases corresponding to different physical situations corresponding to special commutation properties of the time independent Hamiltonians which govern the evolution of $S \oplus E$. Section 5 treats the more general case in which $S$ is evolves under the action of a
time-dependent Hamiltonian inducing the production or absorption of work. In section 6 we develop an application of the formalism developed in section 5 by means of a known model. Finally section 7 contains a summary, conclusions and possible extensions of the results to other developments. Detailed calculations are developed in appendices.

2 The open system

2.1 The time independent system and its environment

Consider a system $S$ and an environment $E$ which acts as a static heat bath, the total system $S \oplus E$ being at thermodynamic equilibrium. The total Hamiltonian reads

$$\hat{H} = \hat{H}_S + \hat{H}_E + \hat{H}_{SE}$$

(1)

where $\hat{H}_{SE}$ defines the interaction between the system $S$ and its environment $E$. We consider here time independent Hamiltonians.

At temperature $T = 0$ the independent systems $S$ and $E$ are described in the bases of states in which they are diagonal

$$\hat{H}_S|n\rangle = e_n|n\rangle$$

$$\hat{H}_E|\nu\rangle = \epsilon_\nu|\nu\rangle$$

(2)

Here $E$ is supposed to be a large system with a fixed number of constituents which exchanges energy with $S$. If the stationary systems $S$ and $E$ share a common finite temperature $T$ we introduce a canonical description of $S$ and $E$ which takes care of this fact and define the spectral function in terms of the eigenstates $\{|\tilde{n}\rangle\}$ of the effective Hamiltonian $\tilde{H}_S$ and $\{|\tilde{\nu}\rangle\}$ of the effective Hamiltonian $\tilde{H}_E$.

The stationary density operators read

$$\hat{\rho}_S = \sum_n |n\rangle p_n \langle n| = \sum_n |n\rangle \frac{e^{-\beta e_n}}{Z_S(\beta)} \langle n|$$

$$\hat{\rho}_E = \sum_\nu |\nu\rangle p_\nu \langle \nu| = \sum_\nu |\nu\rangle \frac{e^{-\beta \epsilon_\nu}}{Z_E(\beta)} \langle \nu|$$

(3)

where $\beta$ is the inverse temperature $T^{-1}$ and $Z_S(\beta)$ and $Z_E(\beta)$ the canonical partition functions in both spaces. The Gibbs states in $E$ will be written

$$|\tilde{\nu}\rangle = \frac{e^{-\beta \epsilon_\nu/2}}{Z_E(\beta)^{1/2}} |\nu\rangle$$

(4)
and a similar expression in $S$ space

$$|\tilde{n}\rangle = \frac{e^{-\beta \epsilon_n/2}}{Z_S(\beta)^{1/2}} |n\rangle \quad (5)$$

In the sequel we shall introduce an effective Hamiltonian in $S$ space, $\tilde{H}_S$ which has to show and verify two central properties:

- it must take care of the presence of the coupling to the environment whether weak or strong.
- it must lead to the determination of the correct thermodynamic functions as mentioned in the introduction.

2.2 The density operator in $S \oplus E$ space

The time dependent matrix elements of the density operator $\hat{\rho}_{SE}(t)$ at $T = 0$ are defined as

$$\rho_{\tilde{k}_1\tilde{k}_2}(t) = \sum_{i_1i_2} a_{i_1\nu_1} a^*_{i_2\nu_2} \langle k_1\nu_3 | e^{-it\hat{H}} | i_1\nu_1 \rangle \langle i_2\nu_2 | e^{it\hat{H}} | k_2\nu_4 \rangle \quad (6)$$

where the $\langle a_{i\nu} \rangle$ coefficients are the entanglement amplitudes of the states in $S \oplus E$. At time $t = 0$

$$\hat{\rho}_{\tilde{k}_1\tilde{k}_2}(0) = a_{\tilde{k}_1\tilde{\nu}_3} a^*_{\tilde{k}_2\tilde{\nu}_4} \quad (7)$$

when the temperature of the system is $T \neq 0$ and the same expression with the states replaced by the corresponding ones given in Eq.2.

Then at $t = 0$ with a system $S \oplus E$ for which $S$ and $E$ are decoupled and we introduce f.i.

$$\hat{\rho}_{\tilde{\nu}_3\tilde{\nu}_4}(0) = c_{\tilde{\nu}_3} c^*_{\tilde{\nu}_4} d_{\tilde{\nu}_3\tilde{\nu}_4} \quad (8)$$

where the $d_{\tilde{\nu}_3\tilde{\nu}_4}$ weigh the states $|\tilde{\nu}_3\rangle, |\tilde{\nu}_4\rangle$ in $E$ space and the coefficients $c_{\tilde{\nu}_i}$ weigh those in $S$ space.

2.3 Time evolution of the density operator

In order to obtain the different quantities defined above one needs to determine the density operator in $S$ space $\hat{\rho}_S(t)$ starting from the expression of the total density operator $\hat{\rho}_{SE}(t)$ whose matrix elements were written out in section 2.1. This will be done by means of the projection of $\hat{\rho}_{SE}(t)$ on $S$ space.

A rigorous expression of this operator for any type of interaction $\hat{H}_{SE}$ and initial conditions (i.e. entangled or non-entangled states) can be obtained in
whole generality relying on previous work [16]. Using the same notations as in section 2.1 it was shown there that the time derivative of the diagonal contributions in $E$ space comes out as

$$\frac{d\hat{\rho}_{ik}^S(t)}{dt} = (-i)[\hat{H}_{\gamma}^d, \hat{\rho}_{\gamma}(t)]^{ik} + (-i)\sum_{\beta \neq \gamma} [\Omega_{\gamma \beta}^{ik}(t) - \Omega_{\beta \gamma}^{ik}(t)]$$

(9)

where $\hat{H}_{\gamma}^d$ is the diagonal part in $E$ space of $\hat{H}$ for fixed $\gamma$ and

$$\Omega_{\gamma \beta}^{ik}(t) = \sum_i (i\tilde{\gamma}|\hat{H}_{SE}|\tilde{\beta} j j) \langle \tilde{\beta} | \hat{\rho}_{SE}(t) | \tilde{\gamma} \rangle$$

$$\Omega_{\beta \gamma}^{ik}(t) = \sum_j (i\tilde{\gamma}|\hat{H}_{SE}(t)|\tilde{\beta} j j) \langle \tilde{j} \tilde{\beta} | \hat{\rho}_{SE}(t) | \tilde{\gamma} \rangle$$

(10)

Integration over time and summation over the $S$ space states $\{\gamma\}$ leads to the matrix elements $\{\rho_{ik}^S(t)\}$. The corresponding Gibbs states are obtained in a basis of states in which $\hat{\rho}_{ik}^S(t)$ is diagonal for $i = k$ and by using Eq.(3). The calculation of the matrix elements of $\hat{\rho}_{ik}^S(t)$ need the use of numerical methods in the general case.

### 2.4 Special cases

The derivation of the previous section Eqs.(9-10) was introduced in order to discuss specific cases of physical interest.

- $[\hat{H}_E, \hat{H}_{SE}] = 0$

  In this case Eq.(9) which governs the evolution of $\hat{\rho}_{ik}^S(t)$ reduces to

$$\frac{d\hat{\rho}_{ik}^S(t)}{dt} = (-i)[\hat{H}_{\gamma}^d, \hat{\rho}_{\gamma}(t)]^{ik}$$

(11)

since $\hat{H}_{SE}$ is diagonal in $E$ in a basis of states in which $\hat{H}_E$ is diagonal. It was shown elsewhere that in this case the time evolution of the system is divisible (semi group property of the propagator) like in a Markov process [20]. One may notice that $S$ and $E$ may be entangled at $t = 0$. A model which verifies the considered condition $[\hat{H}_E, \hat{H}_{SE}] = 0$ can be found in ref. [16]. This is the only case for which an entanglement of $S \oplus E$ at $t = 0$ induces rigorous divisibility and a Markovian evolution of the system $S$ if the interaction between $S$ and $E$ is stochastic.

- $[\hat{H}_S, \hat{H}_{SE}] = 0$
This case corresponds to an adiabatic evolution of the system $S$ which stays in the same state during its time evolution. In a basis of states in which $\hat{H}_S$ is diagonal

\[
\text{Tr}_S \frac{d\hat{\rho}^{ii}_S(t)}{dt} = (-i)\{\text{Tr}_S[\hat{H}_S \otimes \hat{I}_E, \hat{\rho}_{S,\gamma}(t)]^{ii} + [\hat{H}_E \otimes \hat{I}_S, \hat{\rho}_{S,\gamma}(t)]^{ii}\} +

(-i)\text{Tr}_E \sum_\beta \{\langle i\gamma|\hat{H}_{SE}|i\beta\rangle\langle i\beta|\hat{\rho}_{S}(t)|i\gamma\rangle - \langle i\gamma|\hat{\rho}_{S}(t)|i\beta\rangle\langle i\beta|\hat{H}_{SE}|i\gamma\rangle\} \quad (12)
\]

where $\hat{I}_S$ and $\hat{I}_E$ are the unity operators in the corresponding spaces.

3 Thermodynamical description of the stationary system $S$

3.1 The definition of $S$ in the thermodynamic context: effective Hamiltonian for a time-independent system $S$ at equilibrium

Hereafter we follow the method described in [15, 17] and refs. quoted there. In order to get a consistent description of the system $S$ thermodynamically coupled to its heat bath $E$ one needs to introduce an effective Hamiltonian

\[
\hat{H}_S(\beta) = -\beta^{-1} \ln[\tilde{Z}_S \text{Tr}_E(\tilde{\rho}_{SE,\beta})] \quad (13)
\]

where $\tilde{Z}_S = Z_{SE}/Z_E$ is an effective partition function, $Z_{SE}$ the partition function of the total system $S \oplus E$ and $\tilde{\rho}_{SE,\beta}$ the corresponding density operator. These definitions lead to an effective density operator

\[
\tilde{\rho}_{S,\beta} = \frac{e^{-\beta \hat{H}_S}}{Z_S} \quad (14)
\]

For reasons of consistency the present definitions imply the initial condition for which the density operator of $S \oplus E$ is in product form at $t = 0$.

The knowledge of $\hat{H}_S$ and $\tilde{\rho}_S$ allows the construction of the energy and the thermodynamic functions in $S$ space. The new Hamiltonian $\tilde{H}_S$ is a function of the temperature. Hence the internal energy $E_{S,\beta} = -\partial_\beta \ln(\tilde{Z}_S(\beta))$ is given by the expression

\[
E_{S,\beta} = \text{Tr}_S[\tilde{\rho}_{S,\beta}(\hat{H}_S(\beta) + \beta \partial_\beta \hat{H}_S(\beta))] \quad (15)
\]

as well as the free energy $\tilde{F}_{S,\beta} = -\beta^{-1} \ln(\tilde{Z}_S(\beta))$.
\[ \tilde{F}_{S,\beta} = \text{Tr}_S[\tilde{\rho}_{S,\beta}(\tilde{H}_S(\beta) + \beta^{-1}\ln(\tilde{\rho}_{S,\beta}))] \] (16)

and the entropy \[ \tilde{\Sigma}_{S,\beta} = \beta^2 \partial_\beta \tilde{F}_{S,\beta} \]

\[ \tilde{\Sigma}_{S,\beta} = \text{Tr}_S[\tilde{\rho}_{S,\beta}(\beta^2 \partial_\beta \tilde{H}_S(\beta) - \ln \tilde{\rho}_{S,\beta})] \] (17)

The present procedure provides a consistent description of the thermodynamics of open quantum systems. For the explicit derivation of the expressions [15-17] see appendix A.

Relying further on the work of Rivas [15] we consider next the extension to a time-independent systems \( S \) which evolves in time.

### 3.2 Effective Hamiltonian of a system \( S \) evolving in time

In most experimental situations the system \( S \) evolves in time. In this case the equilibrium description above does no longer work and one needs to introduce a time-dependence in the description of \( S \). There has been a long time of confusion in the search of a correct description of the evolution which warrants a correct definition of the thermodynamic functions and the entropy of an open system.

This goal can be reached if \( S \) is governed by an effective Hamiltonian related to \( \hat{H}_S \) of the isolated system through the functional relation [15, 18]

\[ \tilde{H}_S(t, \beta) = -\beta^{-1}(\hat{\rho}_S(t) - \hat{\rho}_S(0)) + \hat{H}_S \] (18)

where \( \hat{\rho}_S(t) \) is the density operator which propagates the system \( S \) coupled to the bath \( E \) through time and, as already mentioned above, consistency implies the specific initial condition

\[ \hat{\rho}_{SE}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_{E,\beta} \] (19)

where \( \hat{\rho}_{E,\beta} \) is the density operator of the stationary heat bath, i.e. no entanglement between \( S \) and \( E \) states.

### 3.3 Thermodynamical description of the time evolving system \( S \)

Using the defined Hamiltonian \( \tilde{H}_S(t, \beta) \) which verifies \( \tilde{H}_S(0, \beta) = \hat{H}_S \) it is easy to derive the expression of the time-dependent internal energy as well as the free energy

\[ E_{S,\beta}(t) = \text{Tr}_S[\hat{\rho}_S(t)[(\tilde{H}_S(t, \beta) + \beta \partial_\beta \tilde{H}_S(t, \beta)]]] \] (20)
\[ \tilde{F}_{S,\beta}(t) = Tr_S[\tilde{\rho}_S(t)(\tilde{H}_S(t, \beta) + \beta^{-1} \ln(\tilde{\rho}_S(t)))] \] (21)

and the entropy of \( S \)

\[ \tilde{\Sigma}_{S,\beta}(t) = Tr_S[\tilde{\rho}_S(t)(\beta^2 \partial_\beta \tilde{H}_S(t, \beta) - \ln(\tilde{\rho}_S(t)))] \] (22)

These expressions can immediately be obtained as an extension of the stationary case by introducing the time dependent effective density operator \( \tilde{\rho}_S(t) \) which will be worked out.

### 3.4 Expressions of the thermodynamic functions at infinite time and thermal equilibrium

At the limit \( t = \infty \) and thermal equilibrium these expressions satisfy the standard expressions

\[ E_{S,\beta}(\infty) = -\partial_\beta \ln Z_S = Tr_S(\tilde{\rho}_{S,\beta} \tilde{H}_S) \] (23)

\[ F_{S,\beta}(\infty) = -\beta^{-1} \ln Z_S \] (24)

\[ \Sigma_{S,\beta}(\infty) = -Tr_S(\tilde{\rho}_{S,\beta} \ln \tilde{\rho}_{S,\beta}) \] (25)

The expressions are worked out in appendix B.

### 3.5 Relative entropy and the second law

The expressions obtained above lead to a consistent thermodynamical description of the evolution of the system \( S \), i.e. they lead to the first and second law.

In particular, starting from the inequality [15]

\[ S[\dot{\rho}_S(t)||\tilde{\rho}_{S,\beta}(t)] \leq S[\dot{\rho}_S(0)||\tilde{\rho}_{S,\beta}] \] (26)

one can derive the thermodynamic inequality

\[ S(t) - S(0) - \beta(E_{S,\beta}(t) - E_{S,\beta}(0)) \geq 0 \] (27)

The expressions are worked out in appendix C.
4 The general case - extension to a time dependent Hamiltonian in $S$ space

We consider now the case for which $\hat{H}_S(t)$ and possibly $\hat{H}_{SE}(t)$ get time-dependent. It is only case in which work can be generated by the system.

4.1 Effective time-dependent Hamiltonian

The generalization of the Hamiltonian in $S$ space [15] leads to the expression of the effective Hamiltonian

$$\tilde{H}_S(t, \beta) = -\beta^{-1}[\hat{\rho}_S(t, \beta) - \hat{\rho}_S(0, \beta)]$$

$$-\beta H_S(0) - \beta \int_0^t ds[\hat{\rho}_S(t, \beta) - \hat{\rho}_S(0, \beta)]d/ds \tilde{H}_S(s) \quad (28)$$

4.2 Internal energy, heat and work

Using the expression of the corresponding internal energy

$$E_{\text{int}}(t) = Tr_S\{\hat{\rho}_S(t, \beta)|\tilde{H}_S(t, \beta) + \beta \partial_\beta \tilde{H}_S(t, \beta)\} \quad (29)$$

where the expression of $\partial_\beta \tilde{H}_S(t, \beta)$ can be straightforwardly worked out.

It is easy to verify that

$$E_{\text{int}}(0) = Tr_S\{\hat{\rho}_S(0, \beta)\tilde{H}_S(0)\} \quad (30)$$

and the heat produced

$$Q(t) = E_{\text{int}}(t) - E_{\text{int}}(0) - \int_0^t ds Tr_S\hat{\rho}_S(\beta, s)d/ds \tilde{H}_S(s) \quad (31)$$

where the last term corresponds to work produced by $S$.

These expressions insure the correctness of the thermodynamic functions.

5 Application to an example: the Jaynes-Cummings model of interaction between atoms and fields

We work out an application of the present formalism with the help of the well known Jaynes Cummings model which describes the evolution of a spinning atom coupled to a single bosonic field.

$$\hat{H} = \hat{H}_S + \hat{H}_{SE} + \hat{H}_E = \omega_a \hat{\sigma}_z + \frac{1}{2} \Omega(\hat{a} \hat{\sigma}_+ + \hat{a}^+ \hat{\sigma}_-) + \omega_c \hat{a}^+ \hat{a} \quad (32)$$
where \((\hat{\sigma}_z, \hat{\sigma}_+, \hat{\sigma}_-\)) are the Pauli matrices, \((\hat{a}, \hat{a}^+)\) bosonic annihilation and creation operators, \((\omega_a, \omega_c)\) and \(\Omega\) energies in units of \(\hbar\).

We consider the particular case for which the spinning atom possesses a time dependent frequency \(\omega_a(t)\) and the same is supposed to be the case for the coupling strength to the field \(\Omega(t)\)

\[
\Omega(t) = f(t)\Omega \\
f(t) = 1 - e^{-\alpha t}
\]

where \(\alpha\) is a real positive constant.

At \(t = 0\) the system \(S\) (the spinning atom) is decoupled from the environment \(E\) (the field) so that the density operator of \(S \oplus E\) factorizes into a product state.

At each time \(|\omega_c - \omega_a(t)| \ll \omega_c + \omega_a(t)\). We use the rotating wave approximation by neglecting the contributions of the small period components \((\omega_c + \omega_a(t))\) and decompose the total Hamiltonian into two parts

\[
\hat{H}(t) = \hat{H}_1 + \hat{H}_2(t)
\]

where

\[
\hat{H}_1 = \omega_c (\hat{a}^+ \hat{a} + \frac{\hat{\sigma}_z}{2})
\]

and

\[
\hat{H}_2(t) = \delta(t) \frac{\hat{\sigma}_z}{2} + \frac{\Omega(t)}{2}(\hat{a} \hat{\sigma}_+ + \hat{a}^+ \hat{\sigma}_-)
\]

with \(\delta(t) = (\omega_a(t) - \omega_c)\).

The spinning atom is supposed to possess a spin projection \(m = 1/2\) and \(m = -1/2\) along the quantization axis.

For a fixed eigenstate \(|n\rangle\) The Hamiltonian \(\hat{H}(t)\) can be diagonalized in a 2 \(\times\) 2 basis of states for each state \(|n, m\rangle\) where the states \(|n\rangle\) are the eigenstates of \(\hat{H}_E\) and \((m = +1/2, -1/2)\) those of \(\hat{\sigma}_z\). The eigenvalues read

\[
E_{n-}(t) = (n + \frac{1}{2})\omega_c - \frac{1}{2}[\delta^2(t) + (n + 1)\Omega^2(t)]^{1/2} \\
E_{n+}(t) = (n + \frac{1}{2})\omega_c + \frac{1}{2}[\delta^2(t) + (n + 1)\Omega^2(t)]^{1/2}
\]

In this basis of states the eigenvectors at time \(t = 0\) are given by

\[
|\Phi_n^-(0)\rangle = -\sin\left(\frac{\alpha_n(0)}{2}\right)|n, m = +1/2\rangle + \cos\left(\frac{\alpha_n(0)}{2}\right)|n + 1, m = -1/2\rangle \\
|\Phi_n^+(0)\rangle = \cos\left(\frac{\alpha_n(0)}{2}\right)|n, m = +1/2\rangle + \sin\left(\frac{\alpha_n(0)}{2}\right)|n + 1, m = -1/2\rangle
\]
with \(\alpha_n(0) = \arctan\left[\frac{\Omega(0)}{\delta(0)}\right]\). At time \(t\)

\[
|\Phi_n^n(t)\rangle = e^{-i \int_0^t dt' E_n^-(t')} |\Phi_n^n(0)\rangle
\]
\[
|\Phi_n^+(t)\rangle = e^{-i \int_0^t dt' E_n^+(t')} |\Phi_n^+(0)\rangle
\]

(39)

are the eigenstates which are normalized to 1. The corresponding Gibbs states read

\[
|\tilde{\Phi}_n^n(t)\rangle = \frac{1}{\sqrt{2}} \left( |\Phi_n^n(t)\rangle - |\Phi_n^+(t)\rangle \right)
\]
\[
|\tilde{\Phi}_n^+(t)\rangle = \frac{1}{\sqrt{2}} \left( |\Phi_n^n(t)\rangle + |\Phi_n^+(t)\rangle \right)
\]

(40)

with Gibbs weight factors

\[
d_{nn,-}(t) = \frac{e^{-\beta E_n^-(t)}}{\sum_n e^{-\beta E_n^-(t)}}
\]

(41)

and a similar expression for \(d_{nn,+}(t)\).

It is now possible to construct the density operator in the 2-dimensional \(S\) space. The diagonal matrix elements read

\[
\rho_{S}^{--}(t, \beta) = \frac{1}{2} \sum_n d_{nn,-}^2(t)
\]
\[
\rho_{S}^{++}(t, \beta) = \frac{1}{2} \sum_n d_{nn,+}^2(t)
\]

(42)

and the non diagonal ones

\[
\rho_{S}^{--}(t, \beta) = \frac{1}{2} \sum_n d_{nn,-}(t)d_{nn,+}(t)e^{-i \int_0^t dt' (E_{n,-}(t') - E_{n,+}(t'))}
\]
\[
\rho_{S}^{++}(t, \beta) = \frac{1}{2} \sum_n d_{nn,+}(t)d_{nn,-}(t)e^{-i \int_0^t dt' (E_{n,+}(t') - E_{n,-}(t'))}
\]

(43)

The knowledge of the density matrix allows the construction of the effective time dependent Hamiltonian (Eq.28) which acts in \(S\) space and last the internal energy of the system (Eq.29). The expression of the effective Hamiltonian \(H_{S}^{\text{eff}}(t)\) acting in \(S\) space is developed in Appendix D.
6 Thermodynamic functions for the case of a time-dependent effective hamiltonian acting in $S$ space

6.1 Internal energy

Using the explicit expression of the effective Hamiltonian in $S$ space given in Appendix D the internal energy comes out as

$$E_{\text{int}}(t, \beta) = \rho_S^+(t, \beta) [\hat{H}_S^+(t, \beta) + \beta \partial \beta \hat{H}_S^-(t, \beta)] + \rho_S^-(t, \beta) [\hat{H}_S^-(t, \beta) + \beta \partial \beta \hat{H}_S^+(t, \beta)] + \rho_S^{++}(t, \beta) [\hat{H}_S^{++}(t, \beta) + \beta \partial \beta \hat{H}_S^{+-}(t, \beta)] + \rho_S^{--}(t, \beta) [\hat{H}_S^{--}(t, \beta) + \beta \partial \beta \hat{H}_S^{+-}(t, \beta)]$$

(44)

6.2 Entropy

The entropy can easily be worked by diagonalization of the density matrix $\hat{\rho}_S(t, \beta)$. This leads to the diagonal matrix elements $\rho_S^{11}(t, \beta)$ and $\rho_S^{22}(t, \beta)$. Then

$$S(t, \beta) = -[\rho_S^{11}(t, \beta) \ln \rho_S^{11}(t, \beta) + \rho_S^{22}(t, \beta) \ln \rho_S^{22}(t, \beta)] + \beta^2 [\rho_S^{+-}(t, \beta) \partial \beta \hat{H}_S^{+-}(t, \beta) + \rho_S^{-+}(t, \beta) \partial \beta \hat{H}_S^{-+}(t, \beta) + \rho_S^{--}(t, \beta) \partial \beta \hat{H}_S^{--}(t, \beta)] + \rho_S^{++}(t, \beta) \partial \beta \hat{H}_S^{++}(t, \beta)$$

(45)

6.3 Free energy

Using the expression introduced in Eq.(21) the free energy is

$$F(t, \beta) = \rho_S^-(t, \beta) [\hat{H}_S^+(t, \beta) + \beta \partial \beta \hat{H}_S^-(t, \beta)] + \rho_S^{+-}(t, \beta) [\hat{H}_S^{+-}(t, \beta) + \beta \partial \beta \hat{H}_S^{-+}(t, \beta)] + \rho_S^{--}(t, \beta) [\hat{H}_S^{--}(t, \beta) + \beta \partial \beta \hat{H}_S^{+-}(t, \beta)] + \rho_S^{++}(t, \beta) [\hat{H}_S^{++}(t, \beta) + \beta \partial \beta \hat{H}_S^{+-}(t, \beta)]$$

(46)

6.4 Work

Work produced by the system $S$ is given by the expression in Eq.(31). It reads

$$W(t, \beta) = \int_0^t ds Tr_S \hat{\rho}_S(\beta, s) d/ds \hat{H}_S(s)$$

(47)

Using the expressions of the density operator in $S$ space given by Eq.(42) and the matrix elements of the Hamiltonian in $S$ space in the same basis of states
\[ H^{++}_S(s) = T_E H^{++}_S(s) \]
\[ H^{++}_S(s) = +1/2\omega_n(s) \cos \alpha_n(s) \] (48)

and
\[ H^{--}_S(s) = T_E H^{--}_S(s) \]
\[ H^{--}_S(s) = -1/2\omega_n(s) \cos \alpha_n(s) \] (49)

one obtains
\[ W(t, \beta) = \int_0^t ds \left[ \rho^{++}_S(s, \beta) d/ds H^{++}_S(s) + \rho^{--}_S(s, \beta) d/ds H^{--}_S(s) \right] \] (50)

### 6.5 Heat

Finally the heat is obtained as
\[ Q(t, \beta) = E_{int}(t, \beta) + 1/2\omega_n(0) - W(t, \beta) \] (51)

### 7 Summary and conclusions

The introduction of thermodynamic concepts in the description of an open quantum system opened many controversial discussions about the consistency of the proposed description with respect to the thermodynamic laws and functions. The difficulties were due to the fact that open systems couple more or less strongly to an environment which generates a major difficulty concerning the definition of the open system itself. These difficulties were overcome very recently \[15, 17\] by means of the introduction of an effective temperature dependent and time-dependent Hamiltonian. This led to a correct formulation of the thermodynamic functions and the thermodynamic laws. Above we developed the essentials of these approaches. We added an explicit and general description of the reduced density operator which governs the open system under consideration. We discussed the case for which the system and its environment are entangled at the beginning of time in a non-stationary scenario necessarily leading to the lack of divisibility in the time evolution of the system as it is the case if the coupling is of stochastic nature \[21, 22\]. Finally we worked out a specific physical example as an application of the formalism. Further developments can be considered, in particular energy transfer between the system and its environment and the study of thermodynamic cycles.

The present description treats the case of a system and its environment which are maintained at fixed temperature all over the time evolution process. This means that the whole device evolves in a thermodynamic equilibrium process.
This may not be necessarily the case in an effective experiment. If stationarity
would not be guaranted non-equilibrium processes would enter and hence a
non-equilibrium thermodynamic description would have to be introduced.

8 Appendix A: The thermodynamic functions
in the stationary case

- Starting from the canonical definition the internal energy reads

\[ E_{S,\beta} = -\partial_\beta \ln(\tilde{Z}_S(\beta)) = (-1)(\tilde{Z}_S(\beta))^{-1}\partial_\beta \tilde{Z}_S(\beta) \]

\[ = -Tr_S[\tilde{\rho}_{S,\beta}e^{\beta \tilde{H}_S(\beta)}] \partial_\beta \tilde{Z}_S(\beta) = -Tr_S[\tilde{\rho}_{S,\beta}(-\beta \partial_\beta \tilde{H}_S(\beta) - \tilde{H}_S(\beta))e^{\beta \tilde{H}_S}] \] (52)

which leads to the expression of eq(15)

\[ E_{S,\beta} = Tr_S[\tilde{\rho}_{S,\beta}(\tilde{H}_S(\beta) + \beta \partial_\beta \tilde{H}_S(\beta))] \] (53)

- The free energy is defined as

\[ \tilde{F}_{S,\beta} = -\beta^{-1} \ln(\tilde{Z}_S(\beta)) = Tr_S[\tilde{\rho}_{S,\beta}(\tilde{H}_S(\beta) + \beta^{-1} \ln \tilde{Z}_S(\beta))] \] (54)

- The entropy is related to the free energy through the relation

\[ \tilde{\Sigma}_{S,\beta} = \beta^2 \partial_\beta \tilde{F}_{S,\beta} = Tr_S[\tilde{\rho}_{S,\beta}(\beta^2 \partial_\beta \tilde{H}_S(\beta) - \ln \tilde{\rho}_{S,\beta})] \] (55)

9 Appendix B: Asymptotic behaviour of the thermodynamic functions

Here we examine the consistence of the definitions of the thermodynamic func-
tions defined above. Under the fixed physical conditions these quantities are
aimed to verify strong asymptotic time related conditions [15].

- At \( t = \infty \) the free energy reads

\[ \tilde{F}_{S,\beta}(\infty) = Tr_S[\tilde{\rho}_{S,\beta}(\infty)(\tilde{H}_S(\beta)(\infty) + \beta^{-1} \ln \tilde{\rho}_{S,\beta}(\infty))] = Tr_S[\tilde{\rho}_{S,\beta}(\infty)(\tilde{H}_S(\beta, \infty) + \beta^{-1} \ln(Z_{SE}/Z_SZ_E)) + \beta^{-1} \tilde{\rho}_{S,\beta}(\infty) \ln \tilde{\rho}_{S,\beta}(\infty)] \] (56)

But

\[ \tilde{H}_S(\beta, \infty) = \tilde{H}_S(\beta) + \beta^{-1} \ln(Z_{SE}/Z_SZ_E) \] (57)
Simplifying this expression
\[ \tilde{F}_{S,\beta}(\infty) = -\beta^{-1} Tr_S[\hat{\rho}_{S,\beta}(\infty) \ln(Z_S)] = -\beta^{-1} \ln(Z_S) \] (58)
and consequently
\[ \tilde{Z}_S(\infty) = Tr_S[e^{-\beta \hat{H}_S(\beta, \infty)}] = Tr_S[e^{-\beta \hat{H}_S}] = Z_S \] (59)

- \text{At } t = \infty
\[ \Sigma_S(\infty) = \beta^2 \tilde{Z}_S(\infty) = \beta^2 \ln Z_S \] (60)

which is a consistent result.

10 Appendix C: Relative entropy

The expected inequality given in Eq.(26) relies on the general expression
\[ S(\hat{\rho}_1||\hat{\rho}_2) = Tr[\hat{\rho}_1 \ln \hat{\rho}_1 - \hat{\rho}_1 \ln \hat{\rho}_2] \] (61)
in Eq.(26) one works the lhs of the inequality
\[ Tr_S[\hat{\rho}_S(t) \ln \hat{\rho}_S(t)] - Tr_S[\hat{\rho}_S(t) \ln \hat{U}_S(t) \hat{\rho}_{S,\beta}] = Tr_S[\hat{\rho}_S(t) \ln e^{-\beta \hat{H}_S(\beta, t)}] \]
\[ = Tr_S[\hat{\rho}_S(t) \ln \hat{\rho}_S(t)] + \beta [Tr_S[\hat{\rho}_S(t) \hat{H}_S(\beta, t)]] \] (62)
where \( \hat{U}_S(t) \) is the time propagator of \( \hat{\rho}_{S,\beta} \).

Subtracting a term \( \beta^2 Tr_S \hat{\rho}_S(t) \ln \hat{\rho}_S(t) \) from the first term and adding it to the second one leads to the lhs of Eq.(22)
\[ S[\hat{\rho}_S(0)||\hat{\rho}_{S,\beta}(t)] = -S(t) + \beta E_{S,\beta}(t) \] (63)
The rhs reads
\[ S[\hat{\rho}_S(0)||\hat{\rho}_{S,\beta}] = Tr_S[\hat{\rho}_S(0) \ln \hat{\rho}_S(0) - \hat{\rho}_S(0) \ln \hat{\rho}_{S,\beta}] \] (64)
Subtracting and adding \( \beta^2 \partial_{\beta} \hat{H}(\beta, 0) \) on the rhs of Eq.(42) leads to
\[ S[\hat{\rho}_S(0)||\hat{\rho}_{S,\beta}] = -S(0) + \beta \hat{H}_S(0) \] (65)
and grouping the expressions together one finally gets
\[ S(t) - S(0) - \beta(E_{S,\beta}(t) - E_{S,\beta}(0)) \geq 0 \] (66)
which proves the consistency of the thermodynamic description of the open system \( S \).
11 Appendix D: Time-dependent effective Hamiltonian acting in $S$ space

Using the expressions of the matrix elements of the density operator (Eqs. 42-43 in section 5) and the conditions imposed to the system at $t = 0$ the matrix elements of the effective Hamiltonian acting in $S$ space in the framework of the Jaynes-Cummings model can be put into the following form

\[ \tilde{H}_S^-(t, \beta) = -\frac{1}{2} \omega_a(t) \]
\[ \tilde{H}_S^+(t, \beta) = \frac{1}{2} \omega_a(t) \] (67)

and

\[ \tilde{H}_S^+(t, \beta) = -\beta^{-1} (\rho^+(t, \beta) - \rho^+(0, \beta)) \]
\[ -\beta \int_0^t (\rho^+(s, \beta) - \rho^+(0, \beta)) d/ds \tilde{H}_S^+(s) ds \] (68)

where $\tilde{H}_S(s)] = 1/2 \omega(s)$ and a similar expression for $\tilde{H}_S^-(t, \beta)$

\[ \tilde{H}_S^-(t, \beta) = -\beta^{-1} (\rho^-(t, \beta) - \rho^-(0, \beta)) \]
\[ -\beta \int_0^t (\rho^-(s, \beta) - \rho^-(0, \beta)) d/ds \tilde{H}_S^-(s) ds \] (69)

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