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Quantum thermodynamical work beyond the Markovian limit

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AUTORIZO A REPRODUÇÃO E DIVULGAÇÃO TOTAL OU PARCIAL DESTE TRABALHO, POR QUALQUER MEIO CONVENCIONAL OU ELETRÔNICO PARA FINS DE ESTUDO E PESQUISA, DESDE QUE CITADA A FONTE.

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Abstract

Extending the principles of thermodynamics to quantum systems composed of one or few elementary parts is one of the key challenges of the field of quantum thermodynamics, with both theoretical and practical interest. In particular, the definition of work for a quantum system strongly coupled to its surroundings is an object of debate in contemporary research. In a recent paper, an approach to this problem has been proposed in the context of a dipole interacting with a single-photon electromagnetic pulse. The method relies on a decomposition of the non-Markovian dynamics of the reduced ensemble, whereby an effective Hamiltonian may be identified. In this monograph, we review and formalize this method, showing for the first time how it can be extended for a general two-level open quantum system, besides reviewing the discussions on the model system to which it was originally applied.

Keywords: Quantum thermodynamics; Non-Markovian dynamics; Non-thermal environments.

1 Introduction

The development of thermodynamics in the 19th century was motivated by the material need of increasingly efficient thermal machines in an industrial-revolutionary context. From such practical problems, a whole new physical theory was born, bringing in two laws that survive to our days as general principels in physics, deeply linked to features of nature as fundamental as the arrow of time. With the later establishment of the atomic hypothesis, statistical mechanics emerged as a successful response to the natural problem of unifying the micro- and macroscopic descriptions of reality. For such a connection to be achieved, the gigantic amount of degrees of freedom underlying macroscopic systems played a key role. These two successful theories, therefore, were bound to find a natural border in the direction of small systems, understood as those composed of *few* elementary parts.

In the past few decades, efforts into extrapolating ideas from the referred theories into the realm of ever smaller systems have led, on the one hand, to the development of a whole new, very vivid branch of physics, namely non-equilibrium statistical mechanics. An important deal of the problems pursued in this field are addressed through a classical-mechanical description of the fundamental interactions, with important achievements, such as the so-called fluctuation theorems, starting with Bochkov and Kuzovlev in 1977 (1) and attaining great popularity after Jarzynski's 1997 work (2). Nevertheless, there exists a class of physical phenomena for which an intrinsically quantum description of the interactions is indispensable. Roughly speaking, this must be the case when one deals with very low

temperatures – when the thermal agitation energy approaches a scale as small as that of quantum transition energies, and eventually quantum correlations may play a non-negligible role. This realm may be referred to as the "quantum regime".

The enterprise of extending the principles of thermodynamics into the quantum regime, as well as understanding the emergence of thermodynamic behavior from quantum-mechanical first principles in the same context, constitute the very active field of Quantum Thermodynamics (QTD). One of the most practical goals underlying this branch of contemporary research is related to the rapid development of quantum technology, up to a point in which even a single atom may play the role of the working entity in a heat engine (3) – although the idea of a quantum thermal machine traces back to a 1959 paper by Scovil and DuBois (4). The chase towards what some call the "quantum revolution" is enough of a motivation for the search for a satisfactory theoretical model of a quantum heat engine. This problem is intrinsically connected to the one of introducing consistent, physically meaningful notions of work – conceived as a useful form of energy – and heat – dissipated energy, related to irreversible processes – in the quantum realm. Broadly speaking, a consensus over such general definitions (specially that of work) has not been reached by the community so far (4, 5), consisting in a contemporary research problem in its own right.

One important cornerstone of QTD was the quantum heat engine model introduced by Alicki in 1979 (6). His approach, which strongly relied on the hypothesis of a weak coupling between the system of interest (*i. e.* the working entity) and its environment (the thermal reservoirs), enabled the introduction of consistent definitions of work and heat, as well as a rigorous proof of the validity of the Second Law of Thermodynamics and, equivalently, of the Carnot bound. This has set the ground for an elegant and consistent approach to QTD, provided the weak-coupling limit is met. Another crucial limitation is that, in such approach, work is not conceived as a genuinely quantum entity: as we shall evidence below (§2), the source of work is necessarily modeled as an external agent which stretches the system's energy levels according to a (presumably) specified protocol.

Recent advances, however, make it latent to pursue an extension of QTD into a *strongly quantum regime* – in which the emergence of quantum correlations in the environment cannot be neglected – and switch to a *totally quantum framework* – whereby all the interacting entities are conceived as quantum systems (4). Another important and correlated feature in this regime is that reservoirs may be found far from equilibrium states (4). For such a general case, there is no consensual or paradigmatic approach to QTD and different attempts to define work have been debated (4, 5). Importantly, even what is to be understood as internal energy is not a trivial question, since a local, physically

meaningful energy observable for strongly coupled systems is not straightforward to identify (7, 8).

Embedded in such a strong-coupling, non-thermal context, in a recent contribution (9), an Alicki-inspired definition of work was introduced and applied to a dipole-photon interaction, with interesting qualitative conclusions. The approach was intrinsically connected to a previously reported ability of splitting the time evolution of the reduced state operator into two parts – one unitary and another non-unitary, *formally resembling* the Markovian master equations upon which Alicki devised his theory –, which provided the identification of an effective Hamiltonian for the system of interest (10). Noticeably, a totally quantum framework is adopted, allowing genuinely quantum phenomena to be studied under a quantum-thermodynamical perspective.

The approach, as addressed in (9), focuses on technical results and lacks a more systematized development of the method, as well as any attempt to generalize it and ponder its features. To achieve those theoretical goals is the main purpose of this monograph, which is structured as follows. In §2, we introduce Alicki's framework of the quantum heat engine, focusing on the essential elements and conclusions. This is to make contrast to the approach of (9), which we detail and develop in §3. In particular, in §3.3, we show that the dynamical splitting addressed there can be achieved for an arbitrary two-level system, with a closed-form expression for the effective Hamiltonian. This is an original contribution of the present work. Then, in §4, we discuss the dipole-photon example, as done in (9), and replicate the main physical discussions. Finally, §5 summarizes our conclusions.

2 The quantum heat engine in Alicki's paradigm

This section is devoted to specifying the context over which Alicki's paradigm of quantum thermodynamics was built, as well as stating the main results obtained therefrom. Such a review is crucial to our work for at least two reasons: *(i)* in its own right, Alicki's theory is a cornerstone of QTD and a thorough understanding of its features and limitations is at the heart of a comprehension of the challenges in the field; *(ii)* the approach to be developed here is largely inspired by the former.

The basic setup behind Alicki's quantum heat engine model, addressed in his seminal work from 1979 (6), consists of a system of interest interacting with a heat bath and a work reservoir. The heat bath is a quantum reservoir in thermal state, weakly coupled to the system of interest. Work, in its turn, is modelled by the explicit introduction of a slowly-varying, time-dependent modification in the system's Hamiltonian. In what follows, we build this setup to further detail, introducing the three elements one at a time and specifying the meaning of "weakly coupled" and "slowly varying" (as

well as the role of those restrictions).

We consider a system S interacting with a heat bath B. The latter is assumed to be in a thermal state[1] at inverse temperature β. (For the remainder of this text we adopt natural units, $k_B = \hbar = c = 1$.) The former has a finite-dimensional Hilbert space and its Hamiltonian, when isolated, is H_S. The fundamental restriction here is that *the coupling between S and B be weak*. In this context, this is equivalent to supposing that the correlation time of B – the characteristic time it takes B to restore its equilibrium state after acted upon by S – be negligible as compared to the typical timescale of S's dynamics (6). This provides the physical validation for approximating the referred dynamics by a quantum dynamical (one-parameter) semigroup (6, 11) or, equivalently, writing a Markovian master equation[2] for $\rho_S(t)$, S's density operator:

$$\mathrm{d}_t\rho_S(t) = -i\left[H_S + \Delta H, \rho_S(t)\right] + \mathcal{L}\left\{\rho_S(t)\right\}. \tag{2.1}$$

Here, d_t stands for time differentiation, ΔH represents the perturbation in the system Hamiltonian due to this weak coupling (also called Lamb correction or Lamb shift) and the superoperator $\mathcal{L}$, called a dissipator, accounts for the non-unitary perturbation on the dynamics (5, 11). Here and to the remainder of this text, we work in the Schrödinger picture.

Now we explicitly introduce a time-dependent term $h(t)$ to the system's Hamiltonian, representing a controlled, external agency. This term is assumed to change very slowly when compared to the bath correlation time. Without such an assumption, the introduction of the driving could destroy the conditions for markovianity; with it, the dynamics is still *locally Markovian*, in the sense that it is Markovian in each time interval within which $h(t)$ does not vary appreciably. Meanwhile, Eq. (2.1) is simply replaced by[3]

$$\begin{aligned} \mathrm{d}_t\rho_S(t) &= -i\left[H(t), \rho_S(t)\right] + \mathcal{L}(t)\left\{\rho_S(t)\right\}, \\ H(t) &:= H_S + h(t). \end{aligned} \tag{2.2}$$

Notice that $\mathcal{L}$ is no longer a constant. The main reason for that is that this dissipator, as it appears in Eq. (2.1), depends functionally on H_S; since that equation is assumed to hold locally in time, upon

[1] Technically, the bath is said to be in a KMS state. For finite-dimensional Hilbert spaces, this reduces to an usual Maxwell-Boltzmann density matrix $\propto \exp\left(-\beta H_B\right)$, while for infinite-dimensional systems (as is the case for heat baths, in this context) the idea is more involved; for details, refer to (11), §3.3.2.

[2] When such an equation is to be derived from first principles, physically equivalent restrictions (*e. g.* the Born-Markov approximation) are always present; for instance, see (11), §3.3.1.

[3] The reader might notice the absence of the bath-induced shift ΔH in the Hamiltonian part. Following (6), we redefine $\mathcal{L}$ so as to include this contribution, which does not modify the crucial mathematical properties of the superoperators, nevertheless resulting in (perhaps slightly) different definitions for U, Q and W in what follows. This is however not a crucial point in the big picture of the theory, which can be adapted so as to include ΔH in $H(t)$, as done in (5).

the substitution $H_S \mapsto H_S + h(t)$, it results that $\mathcal{L}$ will turn out to be a time-dependent superoperator. We could not overemphasize that the time-dependent character of all the operators acting on $\rho_S(t)$ in the right-hand side of Eq. (2.2) *amounts entirely to the time dependence of* $h(t)$.

We are now in a position to introduce the definitions of work and heat adopted in this context. First, the internal energy of the system is defined merely as the mean value of the observable $H(t)$, which rules the unitary part of the dynamics:

$$U(t) := \mathrm{Tr}\left[H(t)\rho_S(t)\right]. \tag{2.3}$$

This quantity may vary either by a change in $H(t)$ or one in $\rho_S(t)$. Informally stating, these two contributions define work and heat, respectively. Using $W(t)$ ($Q(t)$) to denote the total work (heat) received by S from time 0 to time t, the formal definitions are:

$$\mathrm{d}_t W(t) := \mathrm{Tr}\left[\mathrm{d}_t H(t)\rho_S(t)\right]; \tag{2.4}$$

$$\mathrm{d}_t Q(t) := \mathrm{Tr}\left[H(t)\mathrm{d}_t\rho_S(t)\right] \tag{2.5}$$

$$= \mathrm{Tr}\left[H(t)\mathcal{L}(t)\left\{\rho_S(t)\right\}\right]. \tag{2.6}$$

(Eq. (2.6) follows directly from (2.5) with the aid of (2.1).) Those definitions trivially meet the First Law of Thermodynamics, $\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$, since clearly

$$\mathrm{d}_t U(t) = \mathrm{d}_t Q(t) + \mathrm{d}_t W(t). \tag{2.7}$$

What about the Second Law? In the classical realm, for a system undergoing arbitrary processes but whose only external source of heat is a reservoir in equilibrium at temperature β^{-1}, the Law is equivalent to the Clausius inequality, $\Delta S \geqslant \beta Q$, on the entropy change ΔS of the system (12). In the present context, therefore, a good definition of $Q(t)$ should recover this result. Indeed, this is the main achievement of (6). Using some of the most advanced results on quantum dynamical semigroups at the time, Alicki was able to rigorously prove that

$$\mathrm{d}_t S(t) \geqslant \beta \mathrm{d}_t Q(t), \tag{2.8}$$

where $S := -\mathrm{Tr}\left[\rho_S \ln \rho_S\right]$ is the Gibbs-von Neumann (or informational) entropy of the state ρ_S.

The context of (6) was actually a bit more general than the one considered here so far, in that it allowed not just a single but rather a collection of arbitrarily many independent heat baths at (possibly) distinct temperatures. Upon such generalization, all the hypotheses, equations and results stated so far are either unchanged or generalized in an obvious way. In particular, the definitions (2.4) and

(2.5) are the same, and the derived inequality (2.8) has its right-hand side replaced by $\sum_k \beta_k \mathrm{d}_t Q_k(t)$, where $\mathrm{d}_t Q_k(t)$ is the rate of heat intake from the k-th reservoir, which has temperature β_k^{-1}. The single-bath case, adopted here for the sake of clarity, is of course unsatisfactory since a heat engine should operate between (at least) two distinct temperatures.

The two-bath case straightforwardly consists in a heat engine, provided we assume S to return to its initial state after a certain time, defining a cycle. On this setup it is possible to derive the Carnot limit; the task is identical to its classical thermodynamical counterpart, since we formally have the same elements in hand, namely Eqs. (2.7) and

$$\mathrm{d}_t S(t) \geqslant \beta_1 \mathrm{d}_t Q_1(t) + \beta_2 \mathrm{d}_t Q_2(t). \tag{2.9}$$

By integrating equation above and (2.7) in a full cycle, and substituting the latter in the former, the (properly defined) efficiency η is found to satisfy $\eta \leqslant 1 - \beta_1/\beta_2 = 1 - T_2/T_1$. Despite being a simple corollary of Eq. (2.9), this is a sound result, illustrating the power of Alicki's theory.

Let us now synthesize the physical content of this Section. When an open quantum system is only weakly coupled to thermalized reservoirs, and its energy eigenstates and eigenvalues are made to vary slowly by virtue of an external agent, the following take place: *(i)* the dynamics is (locally) Markovian, with unitary and non-unitary parts; *(ii)* the system still has a local, well-defined and unambiguous energy observable, whose mean value provides a neat definition of the thermodynamic internal energy; *(iii)* the change in this energy can be straightforwardly decomposed into two contributions, one from the unitary and another from the non-unitary part of the dynamics; *(iv)* identifying the former as work and the latter as heat, the First Law of Thermodynamics is trivially satisfied and the Second Law can be shown to hold as well.

3 A generalized approach to work and heat

3.1 Motivation

It is now evident how strongly Alicki's approach and results rely on the weak-coupling limit, as well as its intrinsic restriction to what could be labeled as *classical* sources of work (externally controlled parameters). In the present section we attempt to formalize and generalize the method of (9), which is suitable for out-of-equilibrium, strongly-coupled system and reservoir. Besides putting the method in a more explicit framework, with an attempt to touch on its subtleties, we show here that the basic requirements for it to be applied are met by any two-level system of interest.

The point of departure is trying to replicate the form of definitions (2.3), (2.4) and (2.5). The most naive motivation for that is that we want to recover the established definitions in the appropriate limit. Moreover, it is evident that we would automatically recover the First Law. Also, as we shall show, when the reduced system can be assigned a temperature, such a definition of heat would be naturally associated with the entropy intake, which along with the First Law also fixes the definition of work.

Given that we are to maintain the form of Eqs. (2.3) to (2.5), defining work and heat would be a finished task *if there were a well-defined energy observable for the reduced system*. Nevertheless, when it comes to strongly coupled quantum systems, this is far from being the case (7, 8). Even in the Markovian limit, the "bare" Hamiltonian H_S no longer is the generator of the unitary part of the dynamics; indeed, it is broadly established that the coupling with an environment induces a shift in the energy levels (5, 11). Still in the Markovian case, the resort to a master equation of the form of (2.1) provides an unambiguous correction to the original Hamiltonian, since there is a well-defined, time-independent observable associated with the unitary evolution; even a closed-form expression for this correction can be written in terms of the environment observables (11, 13). Now, for a general open evolution, what replaces the right side of Eq. (2.1) is a complicated time integral which does not display an immediate unraveling of unitary and non-unitary contributions (11). Therefore, the procedure of scanning the equation of motion for a Hermitean observable to appropriately replace the isolated system Hamiltonian is not well-defined, in general.

What we shall do here is a subtly different thing. Instead of starting off with the dynamical equation, *i. e.*, a differential equation which determines the (reduced) density operator at arbitrary times given its initial value, we simply begin with the *form* of the density operator itself[4]. By merely differentiating it, we expect to be able to write an equation *formally identical* to (2.2), in which $H(t)$ is a Hermitean operator. We then identify this term as the reduced system's Hamiltonian and proceed as indicated above. So far we have not made clear to any extent that such a decomposition of the time-derivative of the state is feasible at all. We shall show this explicitly for a two-level system in §3.3. For the moment, however, we take this as a hypothesis.

3.2 Definitions

Let S and B be two parts of a composite quantum system, which is described by the Hilbert space $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B$. We denote by $L(\mathcal{H}_S)$ the space of linear operators on $\mathcal{H}_S$ and by $L^2(\mathcal{H}_S)$ that of

[4]We are not looking for a method of solving for the system dynamics – instead, we suppose the evolution to be given (from any of a myriad of existing methods, whether exact or approximate) and use this as our ground.

linear operators on $L(\mathcal{H}_S)$ (super-operators on $\mathcal{H}_S$). The joint system is autonomous, *i. e.*, its global Hamiltonian is time-independent. Therefore we are interested in the exchange of energy *between the parts* S and B. Let the former have a density operator $\rho_S(t) := \mathrm{Tr}_B \rho$, where ρ is the global density operator. As before, S has a Hamiltonian $H_S \in L(\mathcal{H}_S)$ when isolated. Then suppose that the time derivative $\mathrm{d}_t \rho_S(t)$ can be put in the form

$$\mathrm{d}_t \rho_S(t) = -i\left[H(t), \rho_S(t)\right] + \mathcal{L}(t)\left\{\rho_S(t)\right\}, \tag{3.1}$$

where $H(t) \in L(\mathcal{H}_S)$ is a Hermitean observable which commutes with H_S and $\mathcal{L}(t) \in L^2(\mathcal{H}_S)$ is a dissipator, meaning that it can*not* be cast as an imaginary unit times the commutator with some Hermitean operator; in other words, we are supposing that the first term in Eq. (3.1) contains *all* of the unitary contribution to $\mathrm{d}_t \rho_S$. Importantly, a sufficient condition for a given superoperator to be a dissipator is that it be written in the (generalized) Lindblad (or GKSL) form,

$$\mathcal{L}(t)\left\{\rho\right\} = \sum_k \gamma_k(t)\left(A_k(t)\rho A_k(t)^\dagger - \frac{1}{2}\left\{A_k^\dagger(t)A_k(t), \rho\right\}\right), \qquad \gamma_k(t) \in \mathbb{R}, \tag{3.2}$$

which reduces to the usual Lindblad form (Markovian dynamics) upon the further requirement that the γ_k, A_k are constants and $\gamma_k \geqslant 0$[5]. To the remainder of this monograph we shall refer to H and $\mathcal{L}$ as *effective Hamiltonian* and *effective Lindbladian*, respectively. We then define the internal energy S as the mean value of the effective Hamiltonian,

$$U(t) := \mathrm{Tr}\left[H(t)\rho_S(t)\right], \tag{3.3}$$

and work and heat as time-dependent scalar quantities satisfying $W(0) = Q(0) = 0$ and

$$\mathrm{d}_t W(t) := \mathrm{Tr}\left[\mathrm{d}_t H(t)\rho_S(t)\right]; \tag{3.4}$$

$$\mathrm{d}_t Q(t) := \mathrm{Tr}\left[H(t)\mathrm{d}_t \rho_S(t)\right]. \tag{3.5}$$

In order for these definitions to be meaningful we definitely must identify $H(t)$ as the physically observable energy of S. As we have seen, this sort of identification is not trivial in general (§3.1). So far, the only physical motivation for choosing this particular observable is that it figures in the evolution of $\rho_S(t)$ in a way totally analogous to the Hamiltonian part of a Markovian dynamical equation; therefore it is concretely linked to the unitary part of the evolution (if one can think in these terms). This is arguably not enough of a physical justification for such election. At the moment, further justification has been found only on the grounds of a specific physical model (*cf.* §4).

[5]For deeper discussion on this point, one might refer to (14), §IV-B.

To the remainder of this section we take for granted that the effective Hamiltonian has the meaning of physically observable energy of S. Thus the definition (3.3) of internal energy is automatically justified; moreover, definitions (3.3) to (3.5) clearly meet the First Law, $\mathrm{d}_t U = \mathrm{d}_t W + \mathrm{d}_t Q$.

Further validation is provided if one considers, for a moment, a case in which S undergoes a succession of thermal equilibrium states. Although this might sound like the type of restriction we are attempting to avoid here, facts are *(i)* we can still have an arbitrary state for the environment B and *(ii)* this situation may emerge naturally, from a totally autonomous dynamics, *e. g.* in the case of dipole interaction with a single-photon electromagnetic environment (§4). It turns out that, in this situation, the desired link between heat and entropy emerges. From the *formal* point of view, this property is essentially inherited from Alicki's definitions (§2). However, it is instructive to address a proof here, so as to make it clear that it does not depend on any weak-coupling type of assumption. Then, let

$$\rho_S(t) = Z(t)^{-1} \exp\left[-\beta(t) H(t)\right], \tag{3.6}$$

and define

$$S(t) := -\mathrm{Tr}\left[\rho_S(t) \ln \rho_S(t)\right], \tag{3.7}$$

where $Z(t), \beta(t)$ are scalar functions of time. Only for the remainder of this proof, for clarity of notation, we shall drop the time dependencies. We are interested in the entropy change rate,

$$\begin{aligned} \mathrm{d}_t S &= -\mathrm{Tr}\left[\mathrm{d}_t \left(\rho_S \ln \rho_S\right)\right] \\ &= -\mathrm{Tr}\left(\rho_S \, \mathrm{d}_t \ln \rho_S\right) - \mathrm{Tr}\left(\ln \rho_S \, \mathrm{d}_t \rho_S\right). \end{aligned} \tag{3.8}$$

Now, for any diagonalizable operator $X(t)$, it is simple to verify explicitly that $X \mathrm{d}_t \ln X = \mathrm{d}_t X$. The first term in (3.8) is then $-\mathrm{Tr}\left(\mathrm{d}_t \rho_S\right) = -\mathrm{d}_t \mathrm{Tr} \rho_S = 0$, whence

$$\mathrm{d}_t S = -\mathrm{Tr}\left(\ln \rho_S \, \mathrm{d}_t \rho_S\right). \tag{3.9}$$

Now, by taking the logarithm of (3.6) we find $\ln \rho_S = -\beta H - \mathbb{1} \ln Z$, where $\mathbb{1} \in L(\mathcal{H}_S)$ is the identity operator. Substituting this in (3.9) yields

$$\begin{aligned} \mathrm{d}_t S &= \mathrm{Tr}\left[(\beta H + \mathbb{1} \ln Z) \mathrm{d}_t \rho_S\right] \\ &= \mathrm{Tr}\left(\beta H \mathrm{d}_t \rho_S\right) + (\ln Z) \, \mathrm{Tr}\left(\mathrm{d}_t \rho_S\right) \\ &= \beta \, \mathrm{Tr}\left(H \mathrm{d}_t \rho_S\right). \end{aligned} \tag{3.10}$$

Therefore, if we want to recover $\mathrm{d}_t S = \beta \mathrm{d}_t Q$, as expected for a succession of thermal states, it

is natural to define, for this special case, $\mathrm{d}_t Q = \mathrm{Tr}(H \mathrm{d}_t \rho_S)$. As a consequence, given the definition (3.3) of internal energy, that of work (3.4) follows immediately. In other words, even for the case of strong coupling with a non-thermal reservoir, definitions (3.3) to (3.5) have the (presumably unique) feature of preserving the classic thermodynamical relation between heat and entropy change, if the system of interest undergoes a succession of thermal equilibrium states.

3.3 Determination of the effective Hamiltonian

To account for the suitability of the definitions given above, we shall prove that, whenever H_S is two-dimensional (*i. e.* S is a two-level system), it is possible to write $\mathrm{d}_t \rho_S(t)$ in the form (3.1).

We introduce the isolated Hamiltonian H_S and, whenever we use matrix representation, we will be adopting the ordered basis $(|g\rangle, |e\rangle)$ of the eigenstates of H_S. We also introduce the pseudospin operators $\sigma_- := |g\rangle\langle e| = \sigma_+^\dagger$. With no physical loss of generality we can take $H_S|g\rangle = 0$, so that $H_S = \omega_S \sigma_+ \sigma_-$.

We shall pursue our decomposition first for the special case in which ρ_S can be written in the form

$$\rho_S(t) = \begin{pmatrix} 1 - |\psi(t)|^2 & c\psi^*(t) \\ c^*\psi(t) & |\psi(t)|^2 \end{pmatrix}, \tag{3.11}$$

where c is a constant, and later generalize it. This density matrix appears naturally in the case of a number-conserving interaction with a set of oscillator modes, *e. g.* the problem studied in (9) and to be developed below (§4). For this special case, the decomposition we pursue has already been found in (11). Since the method is not explicitly described there, we shall do it here.

Again, we omit time dependencies for clarity. We may eventually use a dot ($\dot{\square}$) for time derivative. By differentiating (3.11) one gets

$$\begin{aligned} \mathrm{d}_t \rho_S &= \begin{pmatrix} -2\mathrm{Re}(\dot\psi\psi^*) & c\dot\psi^* \\ c^*\dot\psi & 2\mathrm{Re}(\dot\psi\psi^*) \end{pmatrix} \\ &= 2\mathrm{Re}(\dot\psi\psi^*)\sigma_z + c\dot\psi^*\sigma_- + c^*\dot\psi\sigma_+, \end{aligned} \tag{3.12}$$

where $\sigma_z := -|g\rangle\langle g| + |e\rangle\langle e|$, as usually. Now the goal is to write the right hand side of (3.12) as a combination of operators composed with ρ_S. In particular, we expect $\sigma_+\sigma_-$ to play a role. It is useful to calculate both its commutator and anticommutator with ρ_S. By direct substitution one finds

$$[\sigma_+\sigma_-, \rho_S] = -c\psi^*\sigma_- + c^*\psi\sigma_+ \tag{3.13}$$

and

$$\{\sigma_+\sigma_-, \rho_S\} = c\psi^*\sigma_- + c^*\psi\sigma_+ + 2\left|\psi\right|^2\sigma_+\sigma_-. \tag{3.14}$$

We now work on the first two terms of (3.12) so as to make the commutator appear:

$$\begin{aligned} c^*\dot{\psi}\sigma_+ + c\dot{\psi}^*\sigma_- &= \frac{\dot{\psi}}{\psi}c^*\psi\sigma_+ + c\dot{\psi}^*\sigma_- \\ &= \frac{\dot{\psi}}{\psi}\left(c^*\psi\sigma_+ - c\psi^*\sigma_-\right) + \frac{\dot{\psi}}{\psi}c\psi^*\sigma_- + c\dot{\psi}^*\sigma_-. \end{aligned} \tag{3.15}$$

The first term above is already proportional to $[\sigma_+\sigma_-, \rho_S]$, but for the "unitary part" of $\mathrm{d}_t\rho_S(t)$ we should have this term multiplied by a purely imaginary function. Then we take the crucial step of decomposing $\dot{\psi}/\psi$ in its real and imaginary parts:

$$\begin{aligned} c^*\dot{\psi}\sigma_+ + c\dot{\psi}^*\sigma_- &= \left(\mathrm{Re}(\dot{\psi}/\psi) + i\mathrm{Im}(\dot{\psi}/\psi)\right)\left(c^*\psi\sigma_+ - c\psi^*\sigma_-\right) + \left(\dot{\psi}/\psi + \dot{\psi}^*/\psi^*\right)c\psi^*\sigma_- \\ &= \mathrm{Re}(\dot{\psi}/\psi)\left(c^*\psi\sigma_+ - c\psi^*\sigma_-\right) + i\mathrm{Im}(\dot{\psi}/\psi)\left[\sigma_+\sigma_-, \rho_S\right] + 2\mathrm{Re}(\dot{\psi}/\psi)c\psi^*\sigma_- \\ &= -i\left[-\mathrm{Im}(\dot{\psi}/\psi)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\psi}/\psi)\left(c^*\psi\sigma_+ + c\psi^*\sigma_-\right); \end{aligned} \tag{3.16}$$

in the second step we used (3.13). Now we may clearly use (3.14) to write

$$c^*\dot{\psi}\sigma_+ + c\dot{\psi}^*\sigma_- = -i\left[-\mathrm{Im}(\dot{\psi}/\psi)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\psi}/\psi)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\left|\psi\right|^2\sigma_+\sigma_-\right). \tag{3.17}$$

We then substitute this identity in (3.12), but first rewrite $\mathrm{Re}(\dot{\psi}\psi^*) = \left|\psi\right|^2\mathrm{Re}(\dot{\psi}/\psi)$; thus

$$\mathrm{d}_t\rho_S = -i\left[-\mathrm{Im}(\dot{\psi}/\psi)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\psi}/\psi)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\left|\psi\right|^2\left(\sigma_+\sigma_- - \sigma_z\right)\right). \tag{3.18}$$

Now we only need to write the last term, $\left|\psi\right|^2\left(\sigma_+\sigma_- - \sigma_z\right)$, as some matrix operation on ρ_S. In matrix representation, $\sigma_+\sigma_- - \sigma_z = \mathrm{diag}\,(1, 0)$, and it is easy to check that $\sigma_-\rho_S\sigma_+ = \mathrm{diag}\left(\left|\psi\right|^2, 0\right)$. We have then shown that, for a density matrix of the form (3.11), the equality

$$\mathrm{d}_t\rho_S = -i\left[-\mathrm{Im}(\dot{\psi}/\psi)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\psi}/\psi)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\sigma_-\rho_S\sigma_+\right) \tag{3.19}$$

holds identically. This is in the form (3.1), with effective Hamiltonian $H(t) := -\mathrm{Im}\left(\dot{\psi}(t)/\psi(t)\right)$.

Now let us drop the assumption on the form of the density operator. Since ρ_S is positive-semidefinite, its diagonal terms are real and nonnegative (in any basis). Then there certainly exists a complex function $\psi(t)$ such that $\langle e|\rho_S|e\rangle = \left|\psi(t)\right|^2$. Besides, we can write the off-diagonal term $\langle g|\rho_S|e\rangle$ as $\zeta(t)\psi^*(t)$, for some complex function $\zeta(t)$[6]. Therefore we have the representation

$$\rho_S(t) = \begin{pmatrix} 1 - \left|\psi(t)\right|^2 & \zeta(t)\psi^*(t) \\ \zeta(t)^*\psi(t) & \left|\psi(t)\right|^2 \end{pmatrix}, \tag{3.20}$$

[6]Given $\langle g|\rho_S|e\rangle$, the value of ζ is simply defined as $\langle g|\rho_S|e\rangle/\psi^*$, if $\psi \neq 0$. Otherwise, $\left|\psi\right|^2 = 0$ and the condition $\rho_S \geqslant 0$ is easily shown to imply $\langle g|\rho_S|e\rangle = 0$ too, so that any finite ζ fits.

in general, and we shall adopt it here. The reason is clear: it becomes natural to generalize the steps taken in the previous case. Since this extension was equivalent to doing $c \mapsto \zeta(t)$, we need only be cautious with the steps in which we *used* that c was a constant; the purely algebraic manipulations remain valid here – in particular, Eqs. (3.13) and (3.14) still hold, upon $c \mapsto \zeta$. Differentiating (3.20),

$$\mathrm{d}_t\rho_S = 2\mathrm{Re}(\dot{\psi}\psi^*)\sigma_z + \zeta\dot{\psi}^*\sigma_- + \zeta^*\dot{\psi}\sigma_+ + \dot{\zeta}\psi^*\sigma_- + \dot{\zeta}^*\psi\sigma_+. \tag{3.21}$$

The first three terms above are identical to those in (3.12) (after $c \mapsto \zeta$); since the steps from (3.12) to (3.19) were merely algebraic we can write here

$$\begin{aligned}\mathrm{d}_t\rho_S = &- i\left[-\mathrm{Im}(\dot{\psi}/\psi)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\psi}/\psi)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\sigma_-\rho_S\sigma_+\right) \\ &+ \dot{\zeta}\psi^*\sigma_- + \dot{\zeta}^*\psi\sigma_+.\end{aligned} \tag{3.22}$$

What is yet to be done is only writing $\dot{\zeta}\psi^*\sigma_- + \dot{\zeta}^*\psi\sigma_+$ as some operation on ρ_S. Through steps strictly analogous to the ones taken from (3.15) to (3.16), we obtain here

$$\dot{\zeta}\psi^*\sigma_- + \dot{\zeta}^*\psi\sigma_+ = -i\left[\mathrm{Im}(\dot{\zeta}/\zeta)\sigma_+\sigma_-, \rho_S\right] + \mathrm{Re}(\dot{\zeta}/\zeta)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\left|\psi\right|^2\sigma_+\sigma_-\right). \tag{3.23}$$

Now by trial and error one finds that

$$\left|\psi\right|^2\sigma_+\sigma_- = \sigma_+\sigma_-\rho_s\sigma_+\sigma_-. \tag{3.24}$$

By substituting back (3.24) to (3.21) we finally have

$$\begin{aligned}\mathrm{d}_t\rho_S = &- i\left[-\mathrm{Im}(\dot{\psi}/\psi - \dot{\zeta}/\zeta)\sigma_+\sigma_-, \rho_S\right] \\ &+ \mathrm{Re}(\dot{\psi}/\psi)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\sigma_-\rho_S\sigma_+\right) \\ &+ \mathrm{Re}(\dot{\zeta}/\zeta)\left(\{\sigma_+\sigma_-, \rho_S\} - 2\sigma_+\sigma_-\rho_s\sigma_+\sigma_-\right),\end{aligned} \tag{3.25}$$

again in the form (3.1)[7]. In principle, given a density matrix $\rho_S(t)$, it is not clear which of the ways of "breaking" its entries into the two functions $\psi(t)$ and $\zeta(t)$ in order to write Eq. (3.20) should be privileged. Thus, it is essential to write the Hamiltonian term (the one that really interests us) in an unambiguous way. Since $\mathrm{Im}z \equiv -\mathrm{Im}z^*$, we can write

[7]Here, to rewrite the last term in the Lindblad form so as to make sure that it is non-unitary (a dissipator), it suffices to note that $(\sigma_+\sigma_-)^\dagger = (\sigma_+\sigma_-)^2 = \sigma_+\sigma_-$.

$$
\begin{aligned}
-\mathrm{Im}(\dot{\psi}/\psi - \dot{\zeta}/\zeta) &= \mathrm{Im}(\dot{\psi}^*/\psi^* + \dot{\zeta}/\zeta) \\
&= \mathrm{Im}\left[(\zeta\dot{\psi}^* + \dot{\zeta}\psi^*)/\zeta\psi^*\right] \\
&= \mathrm{Im}\left[\mathrm{d}_t(\zeta\psi^*)/\zeta\psi^*\right] \\
&= \mathrm{Im}\left[(\mathrm{d}_t\,\langle g|\rho_S|e\rangle)/\,\langle g|\rho_S|e\rangle\right].
\end{aligned}
$$

We have then shown that any 2-level density matrix $\rho_S(t)$ obeys Eq. (3.25), wihch has the form of (3.1) with effective Hamiltonian

$$
H(t) := \mathrm{Im}\left(\frac{\langle g|\mathrm{d}_t\rho_S(t)|e\rangle}{\langle g|\rho_S(t)|e\rangle}\right)\sigma_+\sigma_-. \tag{3.26}
$$

Eq. (3.25) has the sound character of a generalization of (3.19). The latter, as stated previously, is already found in (11), and has been used in our main reference, (9). In both instances, Eq. (3.19) is referred to as an *exact master equation*. One should keep in mind, however, that its physical meaning is not the same as that of a differential equation that could be solved for, *e. g.*, $\psi(t)$ – for this task we still need, in principle, to solve the global equation of motion. From the point of view of the method addressed here, the value of Eq. (3.19) lies in the decomposition of $\mathrm{d}_t\rho_S$ that provides a Hermitean operator $H(t)$ to be identified as the effective Hamiltonian. In this sense, Eqs. (3.25) and (3.26), which we have not found in the literature, have the merit of showing that the approach we convey is, in principle, suitable for an arbitrary two-level open quantum system.

For the synthesis of this Section we have the following. For general coupling between a quantum system and its environment, neither can a Markovian master equation be written, nor is there an obvious redefinition for the physically observable local energy. However, if an equation of the form (3.1) can be written for the derivative of the state operator – which is always the case for a two-level system –, then it is possible to introduce an effective Hamiltonian and consistent notions of internal energy, work and heat. The former, when the system undergoes a succession of thermal states, is consistently connected to a change in its entropy.

4 Dipole in a single-photon reservoir

We now proceed to develop the application of the method of §3 to a concrete physical setup, as done in (9). The system of interest is two-levelled, so we keep the notation of §3.3. As the environment we have a one-dimensional electromagnetic field, described by the creation and annihilation operators $(a_k^\dagger, a_k)$ of the modes labeled by the set of wavenumbers $\{k\}$. Its isolated Hamiltonian is

$H_B = \sum_k \omega_k a_k^\dagger a_k$, where the frequencies satisfy the usual dispersion relation $\omega_k = |k|$.

The interaction Hamiltonian captures the nature of the two-level system (TLS). Two restrictive assumptions are made. First, we regard the TLS as an ideal electric dipole or, equivalently, we work within the dipole approximation; for this reason we may refer to the TLS as "the dipole" as well. The interaction term is then given by $H_{\text{int}} = -dE$, where $d \propto \sigma_+ + \sigma_-$ is the TLS dipole operator and $E = i\sum_k \epsilon_k(a_k - a_k^\dagger)$ is the electric field operator at the position of the TLS, $x = 0$. We also resort to the rotating-wave approximation, which in this case consists in neglecting the term $\sigma_+ a_k^\dagger$ (as well as its conjugate); this is a common assumption in quantum optics when dealing with near-resonant processes (15). We then take $H_{\text{int}} = -\sum_k ig_k(\sigma_+ a_k - \sigma_- a_k^\dagger)$, where $\{g_k\}$ are the coupling constants.

The main feature of the Hamiltonian H_{int} above is that it preserves the global number of excitations: if $N_S = \sigma_+\sigma_-$ and $N_k = a_k^\dagger a_k$ are the number operators, respectively, of the TLS and of the k-th field mode, then the total number of excitations operator $N := N_S + \sum_k N_k$ is such that $[H_{\text{int}}, N] = 0$, as follows from direct substitution. Since H_S and H_B also commute with N, so does the global Hamiltonian $H_{\text{univ.}} = H_S + H_B + H_{\text{int}}$; as a result, N is invariant under time evolution. Therefore, the global state vector $|\xi(t)\rangle$ at arbitrary time t is restricted to the (smallest) eigenspace of N which contains the initially prepared state $|\xi(0)\rangle$.

We are interested in modelling the interaction between the dipole and a *single*-photon pulse. Further assuming the dipole to be initially in its ground state, the global state vector is initially (and, from the reasoning above, permanently) in the one-excitation subspace. At this point, however, we allow a (nonzero) projection in the zero-excitation eigenspace as well. Given this restriction on initial states, the most general form of the global state at any time is[8]

$$|\xi(t)\rangle = c\,|g\rangle\,|0\rangle + \psi(t)\,|e\rangle\,|0\rangle + \sum_k \phi_k(t) a_k^\dagger\,|g\rangle\,|0\rangle\,, \tag{4.1}$$

with $\psi(0) = 0$. Here, $|0\rangle := \bigotimes_k |0_k\rangle$ is the field vacuum state. Now we need the dipole density operator $\rho_S(t) := \text{Tr}_B\left(|\xi(t)\rangle\langle\xi(t)|\right)$, which after some algebra is found to have the exact expression of Eq. (3.11) (11). Thus, its time evolution obeys Eq. (3.19), which has the form (3.1) under the effective Hamiltonian

$$H(t) = \omega(t)\sigma_+\sigma_-, \tag{4.2}$$

where, following (9), we introduced

$$\omega(t) := -\text{Im}\left(\dot{\psi}(t)/\psi(t)\right). \tag{4.3}$$

[8] That $c = \langle g|\,\langle 0|\xi(t)\rangle$ is a constant is also a clear corollary of $[H_{\text{univ.}}, N] = 0$.

We proceed to apply definitions (3.4) and (3.5) to this particular instance. From (3.11) it is immediate to verify that $\mathrm{Tr}\left(\sigma_+\sigma_-\rho_S(t)\right) = |\psi(t)|^2$. Then from $\mathrm{d}_t W(t) = \mathrm{Tr}\left(\rho_S(t)\mathrm{d}_t\omega(t)\sigma_+\sigma_-\right) = \mathrm{d}_t\omega(t)\mathrm{Tr}\left(\sigma_+\sigma_-\rho_S(t)\right) = |\psi(t)|^2\,\mathrm{d}_t\omega(t)$ we have

$$W_{t_1,t_2} = \int_{t_1}^{t_2} |\psi(t)|^2 \left(\mathrm{d}_t\omega(t)\right) \mathrm{d}t; \tag{4.4}$$

similarly,

$$Q_{t_1,t_2} = \int_{t_1}^{t_2} \left(\mathrm{d}_t\,|\psi(t)|^2\right) \omega(t)\mathrm{d}t. \tag{4.5}$$

In order to really study these quantities one needs to know $\psi(t)$, which can only come from the global equations of motion. We now make $c = 0$, which means the problem we really claimed to approach (one excitation only), and then set $H_{\text{univ.}}\,|\xi(t)\rangle = i\mathrm{d}_t\,|\xi(t)\rangle$, with the Hamiltonian $H_{\text{univ.}}$ defined above.[9] With a bit of algebra this equation reduces to

$$\begin{cases} \dot{\psi}(t) = -i\omega_S\psi(t) - \sum_k g_k\phi_k(t); \\ \dot{\phi}_k(t) = -i\omega_k\phi_k(t) + g_k\psi(t), \end{cases} \tag{4.6}$$

as found, for example, in (11). We are interested only in $\psi(t)$. Although it is not difficult to eliminate $\phi_k(t)$ and write a closed-form integro-differential equation for the former, solving it is clearly feasible only within some approximation scheme. Details on the solution, which are typically discussed in quantum optics textbooks, do not add any useful information for our purposes. We shall then only state the result as reported in (10). It lies within the Wigner-Weisskopf approximation, which essentialy assumes that: *(i)* the equation for $\psi(t)$ is local in time; *(ii)* the field has a continuum of modes; *(iii)* both the distribution of these modes and the coupling spectrum g_k display a flat behavior, being constant in a region around ω_S and zero elsewhere. (The nonzero value of g_k we shall denote by g simply.) Another crucial information is the distribution of $\{\phi_k(0)\}$, most conveniently encoded in $\phi(x)$, the real-space wavefunction of the field at $t = 0$ – *i. e.*, the shape of the initial photon packet. The latter is assumed to travel in the positive x direction and to have an exponential profile, as is typical of single-photon sources (10, 9):

$$\phi(x) = NH(-x)\exp\left[\left(\frac{\Delta}{2} + i\omega_L\right)x\right], \tag{4.7}$$

where $H(x)$ is the Heaviside step function, $N := \sqrt{2\pi\rho_0\Delta}$ is a normalization constant, ρ_0 is the

[9] One important subtlety lies beneath this movement of introducing a nonzero c in Eq. (4.1) and later making it zero. Had we written the state vector with $c = 0$ from the beginning, the reduced state (3.11) would have been diagonal, and the steps leading to Eq. (3.19) would not have been able to determine the Hamiltonian part. From the generalized point of view introduced in this monograph, we realize that Eq. (3.26) gives a $0/0$ indeterminacy here. This difficulty is overcome by seeing this degenerate situation as a limiting case of a family of well-behaved ones.

density of modes (in the ω-space) and ω_L and Δ are the parameters that characterize the pulse (central frequency and inverse of typical duration). It is then shown that (10, 9)

$$\psi(t) = \sqrt{\frac{\Gamma\Delta}{2}} \left(\frac{\Gamma - \Delta}{2} - i\delta_L \right)^{-1} \left\{ \exp\left[-\left(\frac{\Gamma}{2} + i\omega_0 \right) t \right] - \exp\left[-\left(\frac{\Delta}{2} + i\omega_L \right) t \right] \right\}, \tag{4.8}$$

where $\Gamma := 4\pi\rho_0 g^2$ is the spontaneous decay rate; $\omega_0 := \omega_S + \omega_{\text{Lamb}}$, and ω_{Lamb} is the Lamb shift calculated from the g_k (*cf.* (10)). For clarity we have introduced here the "detuning" $\delta_L := \omega_L - \omega_0$.

Substituting this in (4.3) yields $\omega(t) = \omega_0 + \delta_{\text{eff}}(t)$, where (10)

$$\delta_{\text{eff}}(t) = \mathrm{d}_t \arctan\left(\frac{\sin(\delta_L t)}{\cos(\delta_L t) - \exp\left[-(\Gamma - \Delta)t/2\right]} \right). \tag{4.9}$$

Thus

$$\mathrm{d}_t\omega(t) = \mathrm{d}_t\delta_{\text{eff}}(t) = \mathrm{d}_t^2 \arctan\left(\frac{\sin(\delta_L t)}{\cos(\delta_L t) - \exp\left[-(\Gamma - \Delta)t/2\right]} \right). \tag{4.10}$$

Now we must evaluate $|\psi(t)|^2$. This is simple algebraic work since we have Eq. (4.8); it yields

$$|\psi(t)|^2 = \frac{\Gamma\Delta}{2} \left[\left(\frac{\Gamma - \Delta}{2} \right)^2 + \delta_L^2 \right]^{-1} \left(e^{-\Gamma t} - 2e^{-(\Gamma+\Delta)t/2} \cos(\delta_L t) + e^{-\Delta t} \right). \tag{4.11}$$

Our interest here is to discuss the application of Eqs. (3.5) and (3.4) to a concrete physical example. To this end, Eqs. (4.9) to (4.11) are what really matters; the details previously given are just the minimal contextualization. Now, let us study the behavior of the amount of work, Eq. (4.4), as a function of the parameters of the incident pulse. At this point we must notice that ω_0 and ω_L are no longer individually relevant, unlike their difference δ_L. So we want to see how $\mathrm{d}_t W$ depends on δ_L and Δ. First, it is evident that $\mathrm{d}_t W$ is an odd function of δ_L; we could say the same of $\mathrm{d}_t\omega_s(t)$. As a consequence, $\mathrm{d}_t W = 0$ for $\delta_L = 0$: the work transfer vanishes at resonance, $\omega_L = \omega_0$. With respect do Δ, it is easily seen from Eq. (4.10) that $\mathrm{d}_t\omega_s(t)$ remains finite as $\Delta \to 0$, and from (4.11) that $|\psi(t)|^2$ vanishes. So W vanishes in this limit as well. Thus we have found the two necessary conditions pointed in (9) for the work transfer to be nonzero: *(i)* off-resonance, $\delta_L \neq 0$; *(ii)* finite bandwidth, $\Delta > 0$. The later, however, is trivial in the sense that, for $\Delta \to 0$, as we just saw, the excited population itself vanishes, so nothing really happens to the TLS.

Now, conditoin *(i)* is more interesting, since for $\delta_L \to 0$ the excitation probability remains finite. In the limit, (4.11) gives $|\psi(t)|^2 \propto \left(e^{-\Gamma t/2} - e^{-\Delta t/2}\right)^2$, while from (4.9) we have $\delta_{\text{eff}}(t) = 0$; so (4.5) gives $\mathrm{d}_t Q = \mathrm{d}_t U \propto \omega_0 \mathrm{d}_t \left(e^{-\Gamma t/2} - e^{-\Delta t/2}\right)^2$. Thus, according to our definitions, there is a nonzero transfer of energy between field and dipole at resonance, amounting totally to heat. It is important to recall that, since $\rho_S(t)$ is a diagonal, two-dimensional density matrix (Eq. (3.11) with $c = 0$), it can always be written in the form (3.6) for some $Z(t)$ and $T(t)$. Thus, the conclusion of §3.2 applies,

and $\mathrm{d}Q = T\mathrm{d}S$ here. Therefore, the proposed effective Hamiltonian allows us to identify, for the pulse-dipole resonant interaction, *an exchange of energy that is totally associated with a change in entropy* and that, correspondingly, is classified as heat. On the other hand, when $\mathrm{d}_t\omega(t)$ is relevant enough – which is indeed achieved for an appropriate choice of δ_L and Δ, as detailed in (10) –, the dominant contribution for $\mathrm{d}_t U$ is that of work, Eq. (4.4).

It should be noted that, in bold terms, Eqs. (4.4) and (4.5) already establish the connections of *(a)* the well-known emission-absorption processes, directly related to a high value of $\mathrm{d}_t\,|\psi(t)|^2$, with heat and of *(b)* the change in $\omega(t)$, identified in (10) as a dynamic Stark shift, with work. The possibility of controlling the interplay between these two terms by suitably tuning the parameters of the incident pulse, as shown above, completes the task of identifying the two quantities introduced by Eqs. (3.4) and (3.5) to two distinct and measurable physical effects. Whether or not these two prescriptions indeed quantify *the exchange of energy* between dipole and photon is a matter that, ultimately, should be answered in the laboratory. From a theoretical standpoint, however, the concrete relation between the underlying Hamiltonian $H(t)$ and a unitary term in the evolution of the state operator, Eq. (3.19), provides a reasonable clue that this should be the case. Furthermore, in (9), an analysis of those quantities is carried also for a coherent incident pulse; comparing the results with those from a semiclassical model reveals that, indeed, at least in this limit, the effective Hamiltonian has the physical meaning of energy of the dipole.

5 Conclusions

In this monograph, we introduced the problem of consistently extrapolating the notion of work into the context of strongly coupled quantum systems, and attempted to describe and develop one recent approach towards its solution. Such problem, which is closely linked to the renormalization of energy in the referred context, consists in one of the central challenges of contemporary quantum thermodynamics, for both theoretical and practical reasons.

The line of analysis we adopted was first addressed in a paper from 2018 (9). There, as we discussed in §4, it was shown that Alicki's Markovian heat engine model, reviewed here (§2), could inspire a definition of work for the problem of a quantum dipole interacting with a single-photon electromagnetic pulse, given the identification of a unitary contribution to the local dynamics, found earlier for the referred problem (10, 11). Moreover, the resulting definitions of work and heat had allowed the authors to link the latter to the emission-absorption process and the former to a frequency

shift in the dipole excitation amplitude. Within the big picture of quantum thermodynamics, this approach has the important quality of providing a fully quantum perspective on work and heat.

Besides replicating the mentioned analysis, this monograph carried out the task of further motivating (§3.1) and formalizing (§3.2) the underlying theoretical approach. From the enterprise of carefully detailing the process of determining the effective Hamiltonian, we naturally developed a generalization of the method, showing that it could be extended for an arbitrary two-level system, regardless of any assumption on its environment (§3.3). Another contribution to the analysis of (9) was the work-entropy relation (§3.2), which is physically meaningful for the particular case considered there. Three natural developments from this line of research would be: *(i)* exploring the consistency between the definitions of work and heat and the Second Law; *(ii)* trying to build a thermal engine setup from the studied dipole-photon model; and *(iii)* using the generalized effective Hamiltonian to study other physical systems, further exploring the consistency of the addressed definitions. This may provide deeper insight to the community on the problem of work in quantum thermodynamics.

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