Qubit thermodynamics far from equilibrium: Two perspectives about the nature of heat and work in the quantum regime

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Considering an entropy-based division of energy transferred into heat and work, we develop an alternative theoretical framework for the thermodynamic analysis of two-level systems. When comparing these results with those obtained using the standard definitions of these quantities, we observe the appearance of a different term of work, which represents the energy cost of rotating the Bloch vector in the presence of the external field that defines the local Hamiltonian. Additionally, we obtain explicit expressions for the temperature, the heat capacity, and the internal entropy production of the system in both paradigms. In order to illustrate our findings we study, from both perspectives, matter-radiation interaction processes for two different systems.

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I. INTRODUCTION

Quantum physics is an intrinsically dynamic theory and therefore time dependence is essential in its description. Classical thermodynamics, on the other hand, mostly considers closed systems that evolve quasiadiabatically [1]. For this reason, when we insert quantum dynamics into thermodynamics we obtain a quantum version of finite-time thermodynamics, which is intimately related to the theory of open systems [2].

Heat and work are the basic mechanisms of energy exchange between thermodynamic systems. From the classical point of view, heat is usually defined as the energy flow which occurs exclusively due to the temperature difference between the systems. Work, on the other hand, is the energy exchange which can be measured through the variation of a macroscopic parameter, such as the volume of the system [1,3-6].

Although for classical thermodynamic systems the classification of the energy transfers as heat and work is not free from controversy, the situation is even more complex when quantum systems are considered. Many nonequivalent definitions of these quantities can be found in the literature [7-13], so the correct identification of heat and work in that regime can be considered an open problem.

One of the most extensively considered paradigms regarding these quantities was proposed by Alicki several decades ago [13]. Defining the internal energy of the system as the expected value of the local Hamiltonian H in the actual reduced state ρ ,

$$E = \langle H \rangle = \operatorname{tr}[H\rho], \tag{1}$$

thus, an infinitesimal energy change takes the form

$$dE = \operatorname{tr}[dH\rho] + \operatorname{tr}[Hd\rho]. \tag{2}$$

The first term on the right-hand side of Eq. (2) is the energy change due to changes in the Hamiltonian of the system, associated with some control parameter which can be modified by the experimenter. Considering the previous discussion about the classical work made on the system, it is reasonable to define the infinitesimal of work as

$$\delta \mathcal{W} = \operatorname{tr}[dH\rho]. \tag{3}$$

Thus, in order to ensure the validity of the first law, the infinitesimal of heat is defined as

$$\delta \mathcal{Q} = \operatorname{tr}[Hd\rho]. \tag{4}$$

Therefore, from this point of view, heat is related to changes in the density matrix describing the quantum state.

Despite its wide application in several contexts [14,15], this approach has some weak points. For example, if we consider two interacting systems with constant local Hamiltonians, Eq. (3) imply that, even if work is done on the global system through a time-dependent Hamiltonian, no work is done on the individual systems, which is counterintuitive.

In this paper we will explore some consequences of a recent proposal that claims to resolve these issues [16,17]. It is based on the hypothesis that the von Neumann entropy is a valid extension of the thermodynamic entropy in the quantum regime and on the fact that it depends only on the eigenvalues λ_i of the density matrix ρ_S [18]:

$$S_{\rm vN} = -\sum_{j=1}^{N} \lambda_j \ln \lambda_j. \tag{5}$$

This implies that the changes in S_{vN} are always accompanied by changes in the eigenvalues of ρ_S . However, classically, the entropy change is proportional to the reversible heat transfer. These observations suggest that heat could not be related to changes in the whole density matrix [see Eq. (4)], but only on its eigenvalues.

The remainder of this paper is organized as follows. In Sec. II we introduce alternative notions of work and heat for a generic finite-dimensional quantum system. In Sec. III, using the above ideas, we develop the complete thermodynamics for a two-level system and we compare the results with those which arise from assuming Alicki's theoretical framework [19]. As we will see, the simplicity of the two-level system allows for a very simple geometric interpretation of the thermodynamic quantities. In Sec. IV we perform both thermodynamic analyses for two specific matter-radiation interaction processes. A summary and some conclusions are presented in Sec. V.

II. ALTERNATIVE PARADIGM

In this section we briefly explain the ideas behind the alternative proposal. First, we note that, in the standard paradigm, Eqs. (3) and (4) are equivalent to

$$\delta \mathcal{W} = \sum_{j} \rho_{jj} dE_j \tag{6}$$

and

$$\delta \mathcal{Q} = \sum_{j} d\rho_{jj} E_j,\tag{7}$$

where $\{E_j\}$ are the eigenenergies of the system and $\{\rho_{jj}\}$ their corresponding probabilities. These expressions are equivalent to those corresponding to the classical notions of work and heat for systems with a discrete spectrum. However, it would be reasonable that quantum features, such as the existence of coherence between the different eigenstates, play an important role, which is not covered by the previous description [20,21].

To analyze the problem from a different perspective, we start by writing the instantaneous spectral decomposition of the density matrix

$$\rho = \sum_{j} \lambda_{j} |\psi_{j}\rangle \langle \psi_{j}|, \qquad (8)$$

where $\{|\psi_j\rangle\}$ are the eigenfunctions and $\{\lambda_j\}$ the set of corresponding eigenvalues. This equation, together with Eq. (1), allows us to express the internal energy as

$$E = \sum_{j} \lambda_{j} \langle \psi_{j} | H | \psi_{j} \rangle, \tag{9}$$

so the infinitesimal energy change is given by

$$dE = \sum_{j} d\lambda_{j} \langle \psi_{j} | H | \psi_{j} \rangle + \sum_{j} \lambda_{j} d \langle \psi_{j} | H | \psi_{j} \rangle.$$
(10)

Recalling Eq. (5), it is clear that only the first term on the right-hand side of Eq. (10) is linked to the entropy change. Thus, it is the only term which should be considered as heat, so we define

$$\delta Q = \sum_{j} d\lambda_{j} \langle \psi_{j} | H | \psi_{j} \rangle \tag{11}$$

and, as a consequence,

$$\delta W = \sum_{j} \lambda_{j} d\langle \psi_{j} | H | \psi_{j} \rangle.$$
(12)

Note that in this paradigm, work is related not only to the possibility of driving the Hamiltonian, but also to the change in the eigenvectors of the density matrix. Of course, for thermal equilibrium states, and more generally for any incoherent state in the energy basis, the Hamiltonian and the density matrix commute. Thus, $\lambda_i = \rho_{ij}$, $\langle \psi_i | H | \psi_i \rangle = E_i$, and, as a consequence, both paradigms are equivalent in that limit.

In the next section we focus on the study of two-level systems, a case which is interesting in its own right due to its technological applications and which, due to its simplicity, allows us to obtain a clear geometrical interpretation of the thermodynamic quantities.

III. THERMODYNAMIC QUANTITIES FOR TWO-LEVEL SYSTEMS IN THE BLOCH VECTOR REPRESENTATION

A. Internal energy, heat, and work

A convenient way to visualize the state of a two-level system is through its Bloch vector

$$\vec{B} = (B_x, B_y, B_z), \tag{13}$$

whose components are, aside from a factor $\hbar/2$, the expected values of the spin operators S_x , S_y , and S_z ,

$$B_{x} = \langle S_{x} \rangle = \operatorname{tr}(\rho_{s}\sigma_{x}),$$

$$B_{y} = \langle S_{y} \rangle = \operatorname{tr}(\rho_{s}\sigma_{y}),$$

$$B_{z} = \langle S_{z} \rangle = \operatorname{tr}(\rho_{s}\sigma_{z}),$$

(14)

where σ_x , σ_y , and σ_z are the Pauli matrices. On the other hand, aside from an irrelevant scalar multiple of the identity, a generic Hamiltonian in two dimensions adopts the form

$$H = -\vec{v} \cdot \vec{\sigma},\tag{15}$$

where \vec{v} can be associated with an effective magnetic field and $\vec{\sigma}$ is a formal vector whose components are the Pauli matrices. In terms of the Bloch vector, the density matrix of a two-level system can be written as

$$\rho = \frac{1}{2} [1 + \vec{B} \cdot \vec{\sigma}]. \tag{16}$$

Using Eqs. (1), (15), and (16) and the identity

$$(\vec{a}\cdot\vec{\sigma})(\vec{b}\cdot\vec{\sigma}) = (\vec{a}\cdot\vec{b})I + i\vec{\sigma}\cdot(\vec{a}\times\vec{b}),\tag{17}$$

we obtain the internal energy

$$E = -\vec{B} \cdot \vec{v}. \tag{18}$$

From Eq. (18) we can write an infinitesimal energy change as

$$dE = -d\vec{B}\cdot\vec{v} - \vec{B}\cdot d\vec{v}.$$
 (19)

1. Standard framework: Paradigm 1

In the standard framework, work is performed on the system only if the Hamiltonian is time dependent. Heat, on the other hand, is related to changes in the quantum state. This point of view leads to the natural definitions of infinitesimal work and heat for a two-level system,

$$\delta \mathcal{W} = -\vec{B} \cdot d\vec{v},\tag{20}$$

$$\delta \mathcal{Q} = -d\vec{B} \cdot \vec{v},\tag{21}$$

in such a way that the first law has the same structure as in the classical case: $dE = \delta Q + \delta W$.

From this point of view, the work is zero when the effective magnetic field is constant in time or when its change is orthogonal to the Bloch vector, i.e., orthogonal to the instantaneous magnetization. Conversely, heat is zero when the Bloch vector is constant in time, i.e., the system is in equilibrium, and also when its change is orthogonal to the effective magnetic field. This situation includes the special case in which the qubit evolves unitarily.

2. Alternative treatment: Paradigm 2

To analyze the problem from this perspective, we first note that the eigenvalues of ρ_S can be written as

$$\lambda_{\pm} = \frac{1}{2} \pm \frac{B}{2},\tag{22}$$

where B is the modulus of the Bloch vector. Therefore, considering Eq. (5), we can write the von Neumann entropy of the qubit as

$$\frac{S_{\rm vN}}{k_B} = -\left(\frac{1+B}{2}\right)\ln\left(\frac{1+B}{2}\right) - \left(\frac{1-B}{2}\right)\ln\left(\frac{1-B}{2}\right).$$
(23)

We note that in the case of two-level systems, the entropy depends only on *B*, so its changes are linked solely to changes in *B*. Thus, from the point of view according to which heat is associated with the energy exchange responsible for entropy change, we conclude that δQ is different from zero if and only if *B* changes.

If we write the energy of the system [Eq. (18)] as

$$E = -B\hat{B}\cdot\vec{v},\tag{24}$$

where \hat{B} is a unit vector in the direction of \vec{B} , the energy change can be partitioned as

$$dE = -dB(\hat{B} \cdot \vec{v}) - Bd(\hat{B} \cdot \vec{v}).$$
(25)

As a result of the previous considerations and since only the first term contributes to the entropy change, we define the heat and work exchanged in this second approach as

$$\delta Q \equiv -dB(\hat{B} \cdot \vec{v}) \tag{26}$$

and

$$\delta W \equiv -Bd(\hat{B} \cdot \vec{v}). \tag{27}$$

It is interesting to consider in detail these expressions. From Eq. (27) we notice that the work done on the system is the product of the modulus of the magnetization *B* and the infinitesimal change in the projection of the effective magnetic field on the direction of the magnetization,

$$\delta W = -Bd(|\vec{v}|\cos\theta), \qquad (28)$$

where θ is the angle between \hat{v} and \hat{B} . Thus, in this framework, work can be performed on the system even if the Hamiltonian, i.e., \vec{v} , is fixed, provided that \hat{B} changes in such a way that the angle between both vectors is not constant in time. In particular, work is extracted from the system, $\delta W \leq 0$, when the Bloch vector changes in such a way that $\hat{B} \cdot \vec{v}$ increases in time, i.e., when \vec{B} tends to align itself with the effective field \vec{v} .

On the other hand, there are two kind of processes for which no heat is exchanged: (i) isoentropic processes, for which B is constant, and (ii) processes for which $\hat{B} \perp \vec{v}$ along the process. This situation includes states that encompass all

possible entropy values, as long as the point representing the reduced state in the Bloch sphere moves on a plane orthogonal to the effective magnetic field. The states located on this plane are the statistical mixtures of the cat states (SMCS) of the instantaneous Hamiltonian and all of them possess zero energy, so if the system transits among these states the work exchanged is also zero.

Regarding the sign of the heat, it is clear that if the angle θ between \hat{B} and \vec{v} satisfies $\theta < \pi/2$, the injection of heat into the system, $\delta Q > 0$, implies an increase in entropy. Conversely, if $\theta > \pi/2$, injection of heat leads to an entropy decrease. This suggests that temperatures associated with states in the upper hemisphere of the Bloch sphere take positive values, while those in the other hemisphere have opposite sign. This point will be studied in detail in the next section.

3. Discussion

The relation between heat and work in the first paradigm, Q and W, and in the second, Q and W, can be obtained as follows. From Eq. (27),

$$\delta W = -Bd(\hat{B} \cdot \vec{v}) = -Bd\hat{B} \cdot \vec{v} - B\hat{B} \cdot d\vec{v}, \qquad (29)$$

and since $-B\hat{B} \cdot d\vec{v} = -\vec{B} \cdot d\vec{v} = \delta \mathcal{W}$ we obtain

$$\delta W = \delta \mathcal{W} - Bd\hat{B} \cdot \vec{v}. \tag{30}$$

Similarly, the relation between the heats exchanged in both paradigms is

$$\delta Q = \delta Q + Bd\hat{B} \cdot \vec{v}. \tag{31}$$

Equation (30) can be written as

$$\delta W = \delta \mathcal{W} + \delta W', \tag{32}$$

where

$$\delta W' = -Bd\hat{B} \cdot \vec{v}. \tag{33}$$

We notice that the work associated with an infinitesimal process in paradigm 2 adds, to the standard contribution δW due to Hamiltonian driving, the additional term $\delta W'$, which is related to the time variation of the density matrix eigenvectors in Eq. (12). Choosing the *z* axis in the direction of \vec{v} and expressing $d\hat{B}$ in spherical coordinates,

$$d\hat{B} = d\theta\hat{e}_{\theta} + \sin\theta d\varphi\hat{e}_{\varphi}, \qquad (34)$$

we find that

$$\delta W' = B \sin \theta \varepsilon d\theta, \tag{35}$$

where $\varepsilon = |\vec{v}|$ is the positive energy eigenvalue.

Since the components of the Bloch vector are proportional to the expected values of the spin operators, \vec{B} can be interpreted as the average magnetic dipole moment of the system, which is embedded in an external magnetic field \vec{v} . For a classical dipole, the potential energy is given by $U = -\vec{B} \cdot \vec{v}$, so it coincides with our expression for the internal energy [Eq. (18)]. Therefore, the work that must be performed against the magnetic field in order to rotate the dipole from the initial to the final configuration equals the potential energy difference between those two configurations.

In our case we notice that, unlike what occurs in unitary evolutions, the interaction with the environment drives the system along trajectories such that the polar angle θ may vary in time, which implies that rotational work must be performed against the magnetic field, in an amount

$$\delta W_{\rm rot} = -\vec{M} \cdot \vec{d\theta},\tag{36}$$

where $\vec{M} = \vec{B} \wedge \vec{v}$ is the torque exerted by the magnetic force and $\vec{d\theta} = d\theta \hat{e_{\varphi}}$. It is now straightforward to show that $\delta W' = \delta W_{\text{rot}}$. Thus, $\delta W'$ is the energetic cost of rotating the dipole in the presence of the external field.

We also notice that $B \sin \theta$ is the coherence of the state measured using the l_1 -norm, C_{l_1} [22],

$$C_{l_1} \equiv \sum_{i \neq j} |\rho_{ij}| = B \sin \theta.$$
(37)

From Eqs. (35) and (37) we obtain

$$\delta W' = C_{l_1} \varepsilon d\theta, \qquad (38)$$

so we conclude that for a fixed local Hamiltonian, work can be performed on the system only if coherence in the energy eigenbasis is present. In fact, from Eq. (38) we see that C_{l_1} can be interpreted as the lever arm of the torque, revealing, in the context of the present work, the role of quantum coherence as a resource for thermodynamic tasks [23,24]. Reciprocally, in Ref. [25] it is shown, employing a differential geometry approach, that the creation of coherence is detrimental to efficiency in finite-time thermodynamic processes.

As a simple example let us consider a qubit undergoing a pure dephasing process. Since the Hamiltonian is fixed, from the point of view of paradigm 1, no work is performed. Since the nondiagonal terms tend to zero while the populations remain constant, the Bloch vector evolves in such a way that the energy of the system does not change. This implies that no heat is exchanged either, so from the point of view of paradigm 1, pure dephasing is a nondissipative process in which the information contained in the coherence is transferred from the system to the environment.

However, information possesses an energy value [26–28], so it should be expected that, despite maintaining its energy constant, the potential of the qubit to do work would decrease. This fact can be explained in a natural way by analyzing the problem from the point of view of paradigm 2. Since during pure dephasing the entropy of the qubit increases, for positive temperature states, heat is transferred to the system. However, since the energy of the system is constant, an equal but opposite amount of work is performed on the environment. This decrease in the ability to perform work can then be interpreted as the result of giving some high-quality energy (work), receiving, in exchange, the same amount of low-quality energy (heat).

B. Temperature

Our main objective so far has been to compare the notions of heat and work within each of the two paradigms considered, However, the adoption of either one allows us to extend, in the case of two-level systems, other thermodynamic quantities to the quantum regime, considering their corresponding classical analogous concepts. Temperature is clearly defined only for systems in thermodynamic equilibrium. Nevertheless, many definitions of temperature have been shown to be useful in nonequilibrium situations [29–37].

The temperatures that we define below should be interpreted as a measure of the entropy changes produced by the heat exchanged when the system finds itself in a particular state. They are not necessarily linked to the direction of the heat flow when thermodynamic systems are put in thermal contact. In fact, it has been theoretically predicted and experimentally shown that the direction of the heat flow between quantum systems in local thermal states can be reversed if quantum correlations are present in the initial state [38,39].

1. Paradigm 1

Consistently with the classical case, we define the temperature of a two-level system as the derivative of the von Neumann entropy with respect to energy in a zero-work process, a condition which is satisfied in the standard framework if the Hamiltonian is time independent. Since the Hamiltonian is determined by the effective magnetic field $\vec{v} = \varepsilon \hat{v}$, fixing the direction \hat{v} we define

$$\frac{1}{\mathcal{T}} = \frac{\partial S_{\rm vN}}{\partial E} \bigg|_{\varepsilon}.$$
(39)

We observe that $S_{\rm vN}$ depends only on *B*, which in turn depends on three arbitrary orthogonal components of the Bloch vector. Due to Eq. (1), the energy depends only on the component parallel to \hat{v} ,

$$E = -\varepsilon \vec{B} \cdot \hat{v}, \tag{40}$$

so we have

$$\frac{1}{\mathcal{T}} = \frac{dS_{\rm vN}}{dB} \frac{\partial B}{\partial (\vec{B} \cdot \hat{v})} \frac{\partial (\vec{B} \cdot \hat{v})}{\partial E} \bigg|_{\varepsilon}.$$
 (41)

From Eq. (23),

$$\frac{dS_{\rm vN}}{dB} = -k_B \tanh^{-1} B, \tag{42}$$

and the other factors are

$$\frac{\partial B}{\partial (\vec{B} \cdot \hat{v})} = \hat{B} \cdot \hat{v}, \quad \frac{\partial (\vec{B} \cdot \hat{v})}{\partial E} \Big|_{\varepsilon} = -\frac{1}{\varepsilon}.$$
 (43)

Thus,

$$\mathcal{T} = \frac{\varepsilon}{k_B(\hat{B} \cdot \hat{v}) \tanh^{-1} B}.$$
(44)

We notice that pure states have zero temperature, except for those such that the Bloch vector is orthogonal to the effective magnetic field, for which the temperature is not defined. In the case of mixed states, the temperature diverges as the magnetization in the direction of \hat{v} goes to zero. This behavior is similar to that corresponding to classical spin systems [40].

2. Paradigm 2

From this perspective, a zero-work process is implemented, keeping constant the product $\hat{B} \cdot \vec{v}$, so we define

$$\frac{1}{T} = \frac{\partial S_{\rm vN}}{\partial E}\Big|_{\hat{B}\cdot\vec{v}} \tag{45}$$

or, equivalently,

$$\frac{1}{T} = \frac{dS_{\rm vN}}{dB} \frac{\partial B}{\partial E}\Big|_{\hat{B}\cdot\vec{v}}.$$
(46)

In this case it is convenient to write Eq. (1) in the form

$$B = -\frac{E}{\hat{B} \cdot \vec{v}} \tag{47}$$

so that the second factor in Eq. (46) is written

$$\left. \frac{\partial B}{\partial E} \right|_{\hat{B}\cdot\vec{v}} = -\frac{1}{\hat{B}\cdot\vec{v}} \tag{48}$$

and therefore

$$T = \frac{\varepsilon \hat{B} \cdot \hat{v}}{k_B \tanh^{-1} B}.$$
(49)

Two families of zero-temperature states appear in paradigm 2: those with B = 1 (pure states) and $\hat{B} \cdot \vec{v} = 0$ (SMCS). On the other hand, the only infinite-temperature state is the maximally mixed state.

3. Discussion

First, we note the different position of the factor $\hat{B} \cdot \hat{v}$ in Eq. (44) (first paradigm) and in Eq. (49) (second paradigm). This implies that the relation between both temperatures is

$$T = \mathcal{T}(\hat{B} \cdot \hat{v})^2 = \mathcal{T}\cos^2\theta, \qquad (50)$$

from which we deduce that they always have the same sign and that, for all possible states, $T \leq \mathcal{T}$. In particular, for incoherent states in the energy eigenbasis ($\theta = 0$) both temperatures coincide:

$$T = \mathcal{T} = \frac{\varepsilon}{k_B \tanh^{-1} B}.$$
 (51)

If additionally the system reaches thermal equilibrium with an environment at temperature T_E , the reduced state is described by the Gibbs state in which the populations of the ground and the excited levels P_g^{eq} and P_e^{eq} are fixed by the environment temperature [41],

$$T_E = \frac{2\varepsilon}{k_B \ln\left(\frac{P_g^{eq}}{P^{eq}}\right)}.$$
(52)

Since in this case the Hamiltonian and the density matrix commute, the populations and the eigenvalues of the density matrix coincide. Therefore, from Eq. (22) we obtain

$$\ln\left(\frac{P_e^{q}}{P_e^{eq}}\right) = \ln\left(\frac{1+B^{eq}}{1-B^{eq}}\right) = 2\tanh^{-1}B^{eq}.$$
 (53)

Finally, from Eqs. (51)–(53) we conclude that, in thermal equilibrium,

$$T = \mathcal{T} = T_E. \tag{54}$$

Therefore, at least in principle, both expressions (44) and (49) extend naturally the concept of temperature to the nonequilibrium situation.

We have already noted that in the context of paradigm 2, the zero-energy plane divides the Bloch sphere into two hemispheres with opposite values of temperature. This is also true in paradigm 1, since both temperatures have the same sign.



FIG. 1. Isothermal surfaces in the Bloch sphere, corresponding to the temperature values $k_B T_1 = \varepsilon$ (red, upper region) and $k_B T_2 = -2\varepsilon$ (blue, lower region) in (a) paradigm 1 and (b) paradigm 2.

This can be seen explicitly in finding the energy-temperature relation from Eqs. (40) and (49),

$$T = -\frac{E}{k_B B \tanh^{-1} B}.$$
 (55)

Finally, we note that in paradigm 1, zero temperature implies zero entropy. This is not true in paradigm 2, since SMCS have zero temperature but their entropy may take any value. Some constant temperature surfaces in both paradigms are shown in Fig. 1.

C. Heat capacity

As usual, we define the heat capacity as the partial derivative of the energy with respect to temperature, in a zero-work process.

1. Paradigm 1

The derivation in Alicki's theoretical framework was performed in Ref. [19],

$$C_{\varepsilon} = \frac{k_B B (1 - B^2) (\tanh^{-1} B)^2 (\vec{B} \cdot \hat{v})^2}{\tanh^{-1} (B) [B^2 - (\vec{B} \cdot \hat{v})^2] (1 - B^2) + B (\vec{B} \cdot \hat{v})}.$$
 (56)

where the consequences of this result are discussed in detail.

2. Paradigm 2

In this approach, the heat capacity is

$$C_{\hat{B}\cdot\vec{v}} = \frac{\partial E}{\partial T}\Big|_{\hat{B}\cdot\vec{v}}.$$
(57)

The evaluation of this equation requires us to express the energy in terms of *T* and $\hat{B} \cdot \vec{v}$. From Eq. (49)

$$B = \tanh\left(\frac{\hat{B}\cdot\vec{v}}{k_BT}\right),\tag{58}$$

which, combined with Eq. (24), leads to

$$E = -(\hat{B} \cdot \vec{v}) \tanh\left(\frac{\hat{B} \cdot \vec{v}}{k_B T}\right).$$
 (59)

Therefore,

$$C_{\hat{B}\cdot\vec{v}} = k_B \left[\frac{x}{\cosh x}\right]^2,\tag{60}$$

where

$$x = \frac{\hat{B} \cdot \vec{v}}{k_B T},\tag{61}$$

and T is given by Eq. (49).

3. Discussion

A quick inspection of Eqs. (56) and (60) shows that in both cases the heat capacity is non-negative for all possible states. The equivalence between Eq. (56) and the equilibrium heat capacity is shown in Ref. [19]. On the other hand, the expression (60) for the heat capacity in the alternative paradigm is clearly a more natural extension of the classical result. Since in thermal equilibrium the Bloch vector is parallel to the effective magnetic field,

$$\hat{B} \cdot \vec{v} = |\vec{v}| = \varepsilon, \tag{62}$$

and since in that case the temperature of the system equals the environment temperature, Eq. (60) reduces to the well-known expression [42]

$$C_{\hat{B}\cdot\vec{v}} = k_B \left[\frac{\varepsilon/k_B T}{\cosh \varepsilon/k_B T} \right]^2.$$
(63)

D. Entropy production

Classically, the entropy change of a closed system is given by

$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}}^{\text{int}},\tag{64}$$

where the first term corresponds to the entropy flux through the system's boundary at temperature T due to heat exchange and the second term is the non-negative entropy production associated with the irreversibilities inside the system [6]. A typical situation is that in which the system is in contact with a heat bath at temperature T_E . In this case, if the system's temperature and the environment temperature are different, an additional entropy production appears due to the irreversible character of the heat transfer. In this case, the total entropy production can be evaluated by applying Eq. (64) to the system plus its border so that the irreversible heat transfer occurs in its interior, i.e., considering the environment temperature instead of the system's temperature in Eq. (64). In this case,

$$dS = \frac{\delta Q}{T_E} + \delta S_{\text{gen}}^{\text{tot}}.$$
(65)

From Eqs. (64) and (65) we can make two important observations. One is that the total entropy production can be separated in the internal and the heat transfer contributions. The latter corresponds to the second term on the right-hand side of

$$\delta S_{\text{gen}}^{\text{tot}} = \delta S_{\text{gen}}^{\text{int}} + \delta Q \left(\frac{1}{T} - \frac{1}{T_E} \right). \tag{66}$$

We also note that Eq. (65) can be written as

$$\delta S_{\text{gen}}^{\text{tot}} = dS - \frac{\delta Q}{T_E}.$$
(67)

Note that the two terms on the right-hand side of this equation correspond to the entropy variations of the system and the environment, respectively, so the total entropy production and the total entropy variation, in the case of classical systems, coincide:

$$\delta S_{\rm gen}^{\rm tot} = dS^{\rm tot}.$$
 (68)

This equation has represented a big challenge to the possibility of extending thermodynamics to the quantum regime. Since the evolution of an open system is, in the general case, irreversible, one expects a positive entropy production $(\delta S_{\text{gen}}^{\text{tot}} > 0)$. However, the unitary evolution of the whole system preserves the density matrix eigenvalues and as a consequence the total entropy does not change $(dS^{\text{tot}} = 0)$. This fundamental problem has been addressed in several works [14,43–45] and it has been suggested that entropy production instead of entropy change is the relevant quantity to explain irreversible behavior. In this work we will only focus on the analysis of Eq. (64) within each paradigm, in order to investigate if an intrinsic entropy production is expected in each case.

1. Paradigm 1

This problem has been analyzed in Ref. [19]. From Eqs. (21), (42), and (44) it is straightforward to obtain an equation linking the von Neumann entropy, the heat transferred, and the temperature defined in Alicki's theoretical framework,

$$dS_{\rm vN} = \frac{\delta Q}{\mathcal{T}} + \delta S_{\rm gen}^{\rm int},\tag{69}$$

where the internal entropy production is given by

$$\delta \mathcal{S}_{\text{gen}}^{\text{int}} = -k_B \tanh^{-1}(B)[\hat{B} - (\hat{v} \cdot \hat{B})\hat{v}] \cdot d\vec{B}.$$
 (70)

Since $\hat{B} - (\hat{v} \cdot \hat{B})\hat{v}$ is orthogonal to \hat{v} , for a unitary evolution, or if the system evolves along equilibrium states, Eq. (70) predicts zero-internal-entropy production, as expected.

2. Paradigm 2

From Eqs. (26), (42), and (49),

$$dS_{\rm vN} = \frac{\delta Q}{T} \tag{71}$$

and, as a consequence,

$$\delta S_{\text{gen}}^{\text{int}} = 0. \tag{72}$$

Thus, in the case of paradigm 2, no intrinsic entropy production is expected in any process. It must be pointed out that this result is valid only in the case of two-level systems. For higher-dimensional systems we have been able to find a very reduced set of quantum states for which the concept of local temperature can be consistently defined, but not a generally valid treatment of this quantity [46].

3. Discussion

To give a physical interpretation of Eq. (70), we first recall the definition of heat in paradigm 1 [Eq. (4)],

$$\delta \mathcal{Q} = -d\vec{B} \cdot \vec{v},$$

and note that only the part of $d\vec{B}$ which is parallel to \hat{v} is responsible for heat exchange. If we restrict ourselves to the

case in which the Hamiltonian is fixed, expressing Eq. (70) in spherical coordinates (with the *z* axis in the direction of \hat{v}), we obtain [19]

$$\delta S_{\text{gen}}^{\text{int}} = -k_B \tanh^{-1} B \sin \theta d(B \sin \theta).$$
(73)

Therefore, the component of $d\vec{B}$ which is orthogonal to \hat{v} and produces no heat is the one responsible for entropy production. Since $B \sin \theta = C_{l_1}$, the entropy produced in paradigm 1 is proportional to the change in the coherence of the qubit in the energy eigenbasis. If coherence is lost, entropy is produced, and destruction of entropy can occur in processes in which the coherence of the qubit increases. On the other hand, the nonexistence of internally generated entropy in paradigm 2 was expected, since in it heat is defined as the part of the energy change which produces an entropy change. Therefore, in this approach, there are no causes of entropy variation other than the heat flow.

The nonexistence of internal entropy production is consistent with the possibility of obtaining an extra amount of work in comparison with the previous approach. Nevertheless, if the system and its environment are at different temperatures, entropy production at the boundary should be expected due to irreversible heat transfer according to Eq. (66),

$$\delta S_{\text{gen}}^{ht} = \delta Q \left(\frac{1}{T} - \frac{1}{T_E} \right). \tag{74}$$

However, this result was obtained by subtracting Eqs. (64) and (65), and it was assumed that the heat released by one system equals the one absorbed by the other, an aspect that in the quantum case is not guaranteed in either of the two paradigms. In fact, for a system of two qubits in positive-temperature states and under a global unitary evolution, the Schmidt decomposition forces both entropy changes to be equal. As a consequence, in paradigm 2 the heat exchanged has the same sign for both systems, so they are releasing or absorbing heat simultaneously.

IV. EXAMPLES

A. Two-level atom in a heat bath

In the Markovian approximation (valid in the hightemperature limit), the evolution of a two-level atom interacting with a thermal state of the electromagnetic field at temperature T_E is given, in the interaction picture, by the master equation [43]

$$\frac{\partial \rho_s}{\partial t} = \gamma_0 (\mathcal{N} + 1) \left(\sigma_- \rho \sigma_+ - \frac{1}{2} \sigma_+ \sigma_- \rho - \frac{1}{2} \rho \sigma_+ \sigma_- \right) + \gamma_0 \mathcal{N} \left(\sigma_+ \rho \sigma_- - \frac{1}{2} \sigma_- \sigma_+ \rho - \frac{1}{2} \rho \sigma_- \sigma_+ \right), \quad (75)$$

where γ_0 is the spontaneous emission rate, ω_0 is the transition frequency, \mathcal{N} is the Planck distribution at that frequency,

$$\mathcal{N} = \frac{1}{e^{\beta_E \hbar \omega_0} - 1},\tag{76}$$

 $\sigma_{\pm} = \frac{1}{2}(\sigma_x \pm i\sigma_y)$, and $\beta_E = (k_B T_E)^{-1}$. It is known that in the asymptotic regime, the equilibrium state of the atom is



FIG. 2. Comparative evolution of the thermodynamic quantities in both paradigms, for a two-level atom interacting with a thermal electromagnetic field at temperature $k_B T_e/\varepsilon = 10$: (a) heat and work exchanged and (b) temperature. In both cases the initial state is a product state, where the atom's initial density matrix is defined by the Bloch vector $\vec{B} = (0.2, 0.5, 0.4)$.

described by the thermal reduced density matrix,

$$\rho^{eq} = \frac{e^{-\beta_E H}}{\operatorname{tr}(e^{-\beta_E H})},\tag{77}$$

which implies that the Bloch vector points in the direction of the effective magnetic field, with modulus

$$B^{eq} = \tanh \beta_E \varepsilon, \tag{78}$$

where $\varepsilon = |\vec{v}|$ is the eigenenergy of the system. As a consequence, the environment temperature determines the equilibrium values of all the thermodynamic quantities. In particular, the equilibrium temperature coincides with the environment temperature.

In the case of paradigm 1, the total energy variation of the atom corresponds to the heat exchanged with the environment, $\Delta E = Q$, represented by the thick red solid line in Fig. 2(a).

From the perspective of paradigm 2, the thermalization process is related to two different phenomena. On the one hand, since the initial entropy of the atom is arbitrary and its final entropy is defined by the environment temperature,



FIG. 3. Evolution of the state of the atom in the Bloch sphere. The system evolves from the initial state (0.2, 0.5, 0.4) (blue point) towards the thermal state (red point) located at the vertical diameter.

a heat exchange is needed so that the final entropy is the one that ensures thermal equilibrium with the environment. On the other hand, work is also required to rotate the Bloch vector towards the equilibrium direction. Both quantities are also represented in Fig. 2(a).

The transient positive character of the work observed in the case of paradigm 2 can be understood by analyzing the path towards the equilibrium state in the Bloch sphere (see Fig. 3). Note that when evolution begins, even though both the distance to the z axis, $B \sin \theta$, and B decrease, θ increases, so work is done on the system. This occurs until the point representing the reduced state reaches the intersection of the trajectory with the tangent line from the center of the sphere (the dashed line in Fig. 3). From that point onward, both B and θ , and consequently the net work, begin to decrease, resulting, at the end of the thermalization process, in a total negative work done on the system. For this reason, thermalization in the case of paradigm 2 requires greater heat absorption from the environment, part of which is converted into work.

The first part of the process described above shows that although coherence is a useful resource, its consumption does not necessarily imply an extraction of work. In fact, if the temperature of the bath is infinite, there are trajectories that converge to the maximally mixed state tangentially to the plane z = 0, so a positive total work is performed on the system during the process.

Regarding the behavior of the temperature, Fig. 2(b) shows that in both theoretical frameworks the temperature increases as the atom absorbs heat. As expected, the respective temperatures tend to the equilibrium temperature, with a faster convergence in Alicki's formulation.

B. Photon exchange between two two-level atoms

As a second example, let us consider a system composed by two two-level atoms embedded in a common environment at zero temperature. If the atoms are separated a distance R and only the spontaneous emission is taken into account, the system undergoes a dissipative process described by the master equation [47]

$$\frac{\partial\rho}{\partial t} = \frac{1}{2} \sum_{k,l=A,B} \gamma_{kl} (2\sigma_-^k \rho \sigma_+^l - \sigma_+^k \sigma_-^l \rho - \rho \sigma_+^k \sigma_-^l), \quad (79)$$

where

$$\sigma_{\pm}^{A} = \sigma_{\pm} \otimes \mathbb{I}_{2}, \quad \sigma_{\pm}^{B} = \mathbb{I}_{2} \otimes \sigma_{\pm}, \tag{80}$$

 $\gamma_{AA} = \gamma_{BB} = \gamma_0$ is the spontaneous emission rate of each atom, $\gamma_{AB} = \gamma_{BA} = \gamma = g(R)\gamma_0 \leq \gamma_0$ is the photon-exchange relaxation constant, and g(R) is a function which approaches the value 1 as $R \rightarrow 0$. In the case $\gamma < \gamma_0$, the atoms are not capable of absorbing all the energy emitted by the other, so independently of the initial state, the composed system asymptotically relaxes towards the ground state $|0\rangle \otimes |0\rangle$.

In Fig. 5 we show the trajectories followed by the states of both atoms in the Bloch sphere. We observe that as the atom A releases energy, its state evolves from its initial state 1A towards the ground state 2A. On the other hand, since atom B starts in the unexcited state 1B, it initially absorbs energy, which drives it out of the ground state. Upon reaching the point 2B, the energy emitted equals the energy absorbed and from that moment on emission exceeds absorption and the atom relaxes to the ground state 3B. In the following we will interpret these facts within the framework of each paradigm.

Let us analyze the case in which the system starts from an initially uncorrelated state, with the atom (A) in the partially excited state defined by the Bloch vector $\vec{B}_A = (0, 0.5, 0.8)$, while atom B is in the ground state, $\vec{B}_B = (0, 0, 1)$. Since the local Hamiltonians are constant in time, from the point of view of paradigm 1 the emission and absorption of photons are modeled as a heat transfer process between the atoms, with some heat released to the environment. The heat exchanged by each atom is represented by the thick red solid lines in Figs. 4(a) and 4(b). We note that in the net balance, the atom A is always releasing heat but at a decreasing rate as it approaches the ground state, while atom B undergoes the process described in the preceding paragraph, interpreting its energy change exclusively as heat absorbed and released.

From the perspective of paradigm 2, the energy variation of atom A includes a negative work component, i.e., work performed by the system, represented by the blue dash-dotted line in Fig. 4(a). This is due to the fact that the angle formed by the Bloch vector and the vertical direction decreases monotonically in time as the atom approaches the ground state. As a consequence, the amount of heat emitted by the atom is less than in paradigm 1.

Regarding atom 2, we note that in the first part of the evolution the photon absorption has two effects. It leads to an increase in entropy, interpreted as heat entering the system. In fact, we note in Fig. 4(c) that the temperature also increases. In addition, it also leads to a change in the direction of the Bloch vector, which moves away from the vertical direction. This motion requires external rotational work to overcome its tendency to stay in the vertical direction due to the presence of the magnetic field. We also note that the signs of heat and work are in phase.



FIG. 4. Thermodynamic quantities for the evolutions of the two atoms considered in Fig. 5 using the two paradigms considered in this work: (a) heat and work exchanged by atom A, (b) the same quantities as in (a) but for atom B, and (c) the respective temperatures, also in both approaches.

As the system subsequently evolves from state 2*B* to 3*B*, the emission of photons governing the process comes from the heat released and work done, in amounts opposite to those of the process $1B \rightarrow 2B$, with a decrease in temperature. It is also interesting to note that the state 2*B* occurs approximately when the temperatures of the atoms are equal, so it is reasonable to think that, from that moment on, the energy flows



FIG. 5. Trajectories in the Bloch sphere. The initial reduced state is a product state of local densities defined by the Bloch vectors $\vec{B}_a = (0, 0.5, 0.8)$ and $\vec{B}_b = (0, 0, 1)$, and $g(R) = \gamma/\gamma_0 = 0.8$. The environment temperature is zero.

between the atoms balance and both atoms cool, releasing energy to the environment, as it can be seen in Fig. 4.

V. FINAL REMARKS AND CONCLUSIONS

In this work we have explored a proposal about the nature of heat and work in the quantum regime, explicitly developing the comparison, for the simple case of a two-level system, of the alternative definitions with one of the more accepted paradigms involving these quantities. In addition to making it possible to reproduce all the classic results for incoherent states, the predictions based on the alternative approach present several advantages with respect to the standard paradigm. In particular, the alternative concept of heat is closer to the classical one, according to which heat is the part of the energy exchange that involves a change in the entropy of the system.

In regard to the definition of work, the main difference in relation to the previous paradigm is the possibility of obtaining work even if the local Hamiltonian of the system does not vary in time. This is consistent with situations in which the interaction with the environment is time dependent, so work is expected to be performed on the system.

In addition, the alternative paradigm allows us to classify the work into two contributions: one associated with Hamiltonian driving, which coincides with the previous definition, and an additional one associated with the coherence of the state of the system. The latter, which does not appear as work in the first paradigm, is related to the work associated with the rotation of the spin direction. This contribution is analogous to the classical work required to rotate a magnetic dipole in an external magnetic field.

Another important advantage of the alternative definition of work is that it highlights the importance of coherence as a resource, an aspect already reported in numerous references. In particular, the analysis of a pure dephasing process from the alternative perspective allows us to understand in a different way why the ability to perform work decreases as the system evolves to the passive state.

A remarkable prediction of the alternative paradigm is that the thermalization process can no longer be understood as being a purely thermal process, but rather involves a mechanical component associated with the change in orientation of the Bloch vector or, in the general case, with a rotation of the eigenstates of the system. However, we must not forget that the notion of heat arises due to the impossibility of accessing the microscopic degrees of freedom of macroscopic systems. It is intuitive that, in the absence of that limitation, many energy exchange processes could be exclusively associated with the concept of work. In the alternative paradigm, heat is linked to a more fundamental inaccessibility, which is a consequence of the quantum description of open systems in terms of mixed states.

Finally, a counterintuitive aspect of paradigm 1 that is not resolved by the alternative proposal has to do with the fact

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that, since heat and work are defined using local variables, they cannot be considered energy flows in a strict sense. In the general case, the heat released by one part of the system can be different from the heat absorbed by the other, and the same occurs with the work. Maybe these concepts can be defined unambiguously and respecting all the intuitive requirements, only in particular situations, such as those in which the system of interest interacts with systems which, by construction, can only exchange either heat or work in the classical sense.

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