# Carnot's theorem for nonthermal stationary reservoirs

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Carnot's theorem poses a fundamental limit on the maximum efficiency achievable from an engine that works between two reservoirs at thermal equilibrium. We extend this result to the case of arbitrary nonthermal stationary reservoirs, even with quantum coherence. In order to do this we prove that a single nonthermal reservoir is formally equivalent to multiple equilibrium ones. Finally, we discuss the possibility of realizing an engine that works at unit efficiency by exploiting quantum coherence present in the reservoir.

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## I. INTRODUCTION

For almost two centuries, Carnot's theorem has constituted one of the cornerstones of thermodynamics, setting a fundamental bound on the efficiency of any heat-to-work conversion process. It states that *all reversible engines working between two reservoirs at temperatures $T_C$ and $T_H$ have the same efficiency $\eta_C = 1 - \frac{T_C}{T_H}$. No engine working between two reservoirs at thermal equilibrium can have an efficiency greater than that*. Here the efficiency is defined as the ratio between $W$, the work performed by the engine, and $Q_H$, the heat extracted from the hotter reservoir.

In this paper we generalize Carnot's theorem to a more general setting in which the reservoirs are not in thermal equilibrium (and thus $T_C$ and $T_H$ cannot be defined). In the field of quantum thermodynamics, examples of such nonthermal reservoirs can be found, for example, in the study of engines with strongly coupled [1] or quantum coherent [2] reservoirs. While in the following we concentrate on this kind of *microscopic* example, it is noteworthy that, in general, most of the engines present in our everyday world actually extract energy from nonequilibrium environments (e.g., all living being extracting energy from ATP molecules).

This paper is structured as follows: in Sec. II we start by introducing our approach to heat engines, which we then use in Sec. III to rederive the standard Carnot's theorem. In Sec. IV we prove a general equivalence theorem, stating that a nonthermal reservoir is formally equivalent to a collection of equilibrium ones at different temperatures. This result is used in Sec. V to prove a generalized version of Carnot's theorem, valid for general nonthermal reservoirs. In Sec. VI this theorem is tested against some previously known results. Finally, using the developed theory, in Sec. VII, we discuss the possibility of realizing an engine exploiting quantum coherence to work at unit efficiency. Conclusions and perspectives are drawn in Sec. VIII.

## II. GENERAL THEORY

In developing our program we are immediately confronted with the problem of defining what we mean by *reservoir*. In order to keep our theory as general as possible, we consider the broadest possible definition of reservoir, that is, we consider a reservoir to be a completely general physical system, with the only constraint that its size and the strength of the interaction with the external world (the engine in our case) are such that its state is not affected noticeably by the time evolution.

The generality of the above definition implies that we disregard any *a priori* difference between a heat reservoir and a work reservoir. The difference will only be *a posteriori*. If our theory implies that it is possible to extract work by coupling the engine with only one reservoir, we classify it as a work reservoir. A typical example is an inverted system, such that a higher-lying energy level has a larger population than a lower-lying one. It is well known that energy can be extracted from such systems without any need for a second reservoir (e.g., a laser extracts energy from an inverted medium).

While the formalism we develop could be used to describe such systems, it is not meaningful to define an efficiency in the usual sense for them (by energy conservation $W = Q_H$ and thus $\eta = 1$). We thus disregard such systems because Carnot's theorem does not apply to them. When, in the following, we talk about *heat* engines, we imply engines working with reservoirs defined in such a sense.

To formulate our theory in a model-independent manner, we adopt a slightly unusual approach to the study of heat engines. Heat engines are normally studied taking into consideration some of their degrees of freedom, evolving under the influence of two (or eventually more) external reservoirs. Given that an engine is, by definition, cyclical, after a cycle the engine is back to its initial state while the reservoirs have slightly evolved. We can thus model the action of the engine as an operator coupling the reservoirs and allowing energy flows between them (see Fig. 1 for a schematic representation of the two approaches). This point of view will allow us to consider arbitrary reservoirs, be they at thermal equilibrium or not, and to optimize the efficiency of the engine over the space of all the possible interaction operators (i.e., all the possible engines).

In our theory, the reservoirs are thus dynamical objects and we describe them in terms of their density operators $\rho_H$ and $\rho_C$ and Hamiltonians $H_H$ and $H_C$, whose eigenvalues we call $E_H$ and $E_C$. Given that the reservoirs can *a priori* be nonthermal, the subscripts $H$ (hot) and $C$ (cold) have no direct implication of their temperatures but, rather, are used to differentiate the energy source (hot reservoir) and drain (cold reservoir). In order to derive our main results, we restrict our attention to the

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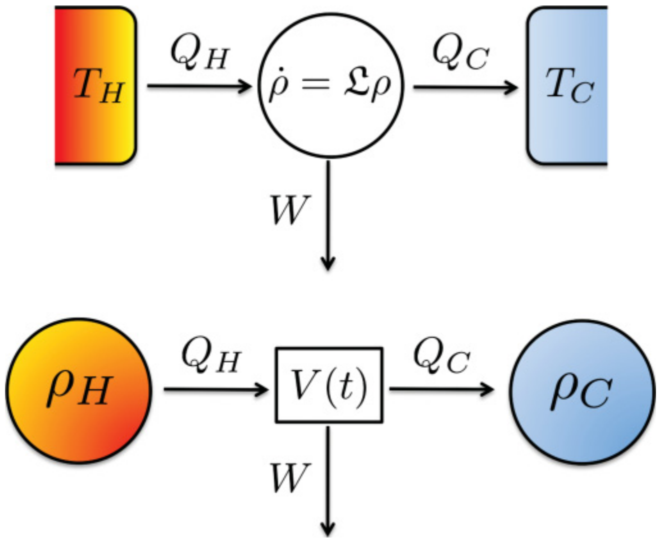


FIG. 1. (Color online) Top: Standard approach in the study of heat engines. The engine's degrees of freedom evolve under the influence of fixed reservoirs (e.g., through some form of Liouvillian operator $\mathfrak{L}$). Bottom: The approach proposed in this paper. The reservoirs represent the dynamical degrees of freedom of the theory, and they evolve under the effect of coupling $V(t)$ mediated by the engine.

case in which the initial states of the decoupled reservoirs are time independent, that is,

$$[H_C,\rho_C] = [H_H,\rho_H] = 0. \tag{1}$$

The engine's effective role is to couple the two reservoirs. It can thus be described completely by a Hermitian time-dependent coupling operator $\lambda V(t)$, where $\lambda \in \mathbb{R}$ and $V(t)$ is an operator over the tensor product of the Hilbert spaces of the two reservoirs (without the time dependence the engine would conserve the total energy of the reservoirs and thus extract no work).

In the definition of reservoir we chose, it is explicitly required that its state does not change in any significant way during the interaction with the engine. For this reason, to recover the usual thermodynamic results with our approach, we have to consider the limit of vanishing interaction $\lambda \to 0$, thus developing the theory of the first nonvanishing order in $\lambda$. This limit is well defined because the efficiency, which is given by the ratio between work and heat fluxes, will not depend on $\lambda$.

In the interaction picture, the Liouville equation for the system, up to the second order, takes the form

$$\dot{\rho}(t) = i\lambda[\rho(0),\tilde{V}(t)] - \lambda^2 \int_0^t [[\rho(0),\tilde{V}(\tau)],\tilde{V}(t)]d\tau, \tag{2}$$

where $\tilde{V}(t) = e^{it(H_H+H_C)}V(t)e^{-it(H_H+H_C)}$ is the perturbation in the interaction picture and $\rho(0) = \rho_H \otimes \rho_C$ is the initial density matrix. In order to calculate the heat flow from reservoir $j = \{C,H\}$, we can use the quantum version of the first law of thermodynamics [3]. The total internal energy of reservoir $j$ is given by

$$U_j = \text{Tr}(\rho(t)H_j), \tag{3}$$

and thus its time variation is

$$\dot{U}_j = \text{Tr}(\rho(t)\dot{H}_j) + \text{Tr}(\dot{\rho}(t)H_j). \tag{4}$$

The two terms on the right-hand side of Eq. (4) can be identified, respectively, as the exchanged work and heat, making Eq. (4) a quantum version of the first law of thermodynamics. The interested reader is invited to read Ref. [3] and references therein for a discussion of the relevance of this identification. In our case the Hamiltonian of the reservoirs is time independent and thus they exchange no mechanical work. The exchanged heat, which in the present case is equal to the total energy variation, can thus be calculated as

$$\dot{Q}_j(t) = -\text{Tr}(\dot{\rho}(t)H_j), \tag{5}$$

where we have chosen the convention that $Q_j$ is positive if heat is extracted *from* the reservoir. Inserting Eq. (2) into Eq. (5) we have

$$\dot{Q}_j(t) = -i\lambda\text{Tr}([\rho(0),\tilde{V}(t)]H_j) + \lambda^2 \int_0^t \text{Tr}([[\rho(0),\tilde{V}(\tau)],\tilde{V}(t)]H_j)d\tau, \tag{6}$$

where the first term on the right-hand side vanishes due to Eq. (1). Formally integrating Eq. (6) up to final time $t_f$, chosen to be a multiple of the engine period, we obtain the total amount of heat exchanged with each reservoir,

$$Q_j = \frac{\lambda^2}{2}\text{Tr}([[\rho(0),M],M]H_j), \tag{7}$$

where

$$M = \int_0^{t_f} \tilde{V}(t)dt, \tag{8}$$

and we have exploited the fact that, using the Jacobi identity and the fact that the initial states of the decoupled reservoirs are time independent [Eq. (1)], we have, for $\forall t_1,t_2$,

$$\text{Tr}([[\rho(0),\tilde{V}(t_1)],\tilde{V}(t_2)]H_j) = \text{Tr}([[\rho(0),\tilde{V}(t_2)],\tilde{V}(t_1)]H_j). \tag{9}$$

The net balance of energy between the two reservoirs gives the total work extracted by the engine,

$$W = Q_H + Q_C. \tag{10}$$

Introducing indexes $(p,q)$ over the energy eigenstates of the cold reservoir and $(m,n)$ over the eigenstates of the hot one, and noticing that, because of Eq. (1), $\rho_C$ and $\rho_H$ can be made diagonal in such a basis, we can rewrite Eq. (7) elementwise as

$$\begin{aligned} Q_C &= \lambda^2 \sum_{m,n,p,q} \left|M_{mp}^{nq}\right|^2\left(\rho_H^m\rho_C^p - \rho_H^n\rho_C^q\right)E_C^p, \\ Q_H &= \lambda^2 \sum_{m,n,p,q} \left|M_{mp}^{nq}\right|^2\left(\rho_H^m\rho_C^p - \rho_H^n\rho_C^q\right)E_H^m. \end{aligned} \tag{11}$$

Exploiting the hermiticity of $M$ ($|M_{mp}^{nq}| = |M_{nq}^{mp}|$), we can rewrite Eq. (11) summing only over states such that $E_H^m > E_H^n$, thus obtaining

$$Q_C = \lambda^2 \sum_{\substack{m,n,p,q\\E_H^m > E_H^n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_C^p - E_C^q\right),$$
$$Q_H = \lambda^2 \sum_{\substack{m,n,p,q\\E_H^m > E_H^n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_H^m - E_H^n\right). \tag{12}$$

Equation (12) gives a self-contained, model-independent description of energy exchanges in a general heat engine. The explicit dependence over the Hamiltonian spectrum makes this formalism particularly adapted to the study of the engine efficiency at the ultimate quantum limit [4–6].

## III. STANDARD CARNOT'S THEOREM

It is interesting to note that the standard Carnot's theorem can be easily derived from Eq. (12), by choosing properly normalized thermal distributions for the reservoirs

$$\rho_H^m = e^{-E_H^m/T_H}/Z_H, \quad \rho_C^p = e^{-E_C^p/T_C}/Z_C, \tag{13}$$

with $T_H \geqslant T_C$. In order to have the engine extract heat from the hot reservoir ($Q_H \geqslant 0$), from Eq. (12) we need to have the condition

$$\rho_H^m \rho_C^p - \rho_H^n \rho_C^q \geqslant 0, \tag{14}$$

verified at least for some values of $(m,n,p,q)$ (please refer to Appendix for a detailed justification of this important point). Using the reservoirs in Eq. (13), Eq. (14) becomes

$$\frac{E_C^q - E_C^p}{E_H^m - E_H^n} \geqslant \frac{T_C}{T_H}. \tag{15}$$

Writing down the engine efficiency using Eqs. (10) and (12), we have

$$\eta = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} \tag{16}$$
$$= 1 - \frac{\sum_{\substack{m,n,p,q\\E_m > E_n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_C^q - E_C^p\right)}{\sum_{\substack{m,n,p,q\\E_m > E_n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_H^m - E_H^n\right)}.$$

It is easy to verify that any value of $(m,n,p,q)$ that does not satisfy Eq. (14) lowers the overall efficiency $\eta$. We can thus rewrite Eq. (16) as

$$\eta \leqslant 1 - \frac{\sum'_{\substack{m,n,p,q\\E_m > E_n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_C^q - E_C^p\right)}{\sum'_{\substack{m,n,p,q\\E_m > E_n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_H^m - E_H^n\right)}, \tag{17}$$

where the prime over the sum symbol means that we sum only over indexes such that Eq. (14) is satisfied.

By construction, each term in the sum in the numerator of Eq. (17) obeys the inequality in Eq. (15). We can thus fix a lower bound on each of the terms and obtain Carnot's result,

$$\eta \leqslant 1 - \frac{T_C}{T_H}. \tag{18}$$

If all the transitions take place between almost-equilibrium states, the left-hand side of Eq. (14) tends toward 0 and Eqs. (15) and (18) become equalities. This is independent from the chosen engine interaction $M_{mp}^{nq}$, because each term $|M_{mp}^{nq}|^2(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q)$ in Eq. (12), being present in both $Q_C$ and $Q_H$, simplifies in Eq. (18). That is, consistently with the usual formulation of Carnot's theorem, we find that any engine working between states almost at equilibrium attains Carnot efficiency,

$$\eta_C = 1 - \frac{T_C}{T_H} \tag{19}$$

(a similar approach to the Carnot efficiency has recently been proposed in Ref. [5]). The fact that we can prove Carnot's theorem from our formalism is not surprising, because systems at thermal equilibrium [like the reservoirs in Eq. (13)] are known to obey it. This is a good consistency check for our approach.

## IV. RESERVOIR EQUIVALENCE THEOREM

If the reservoirs' distributions differ from thermal equilibrium ones, we cannot in general define a temperature for them, and thus Eq. (18) does not apply. In this section we prove a reservoir equivalence theorem that we use in Sec. V to establish a generalized form of Carnot's theorem, valid for arbitrary nonthermal reservoirs.

We start by rewriting the sum in Eq. (12) as a sum over all the possible transitions between pairs of states in each reservoir:

$$Q_C = \lambda^2 \sum_{\substack{m \to n\\E_m > E_n}} \sum_{p \to q} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_C^p - E_C^q\right),$$
$$Q_H = \lambda^2 \sum_{\substack{m \to n\\E_m > E_n}} \sum_{p \to q} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_H^m - E_H^n\right). \tag{20}$$

From Eq. (20), we see that the heat flow between the two reservoirs is composed of the sum over all the possible pairwise interactions, coupling a transition in the cold reservoir (from $p$ to $q$) and a transition in the hot one (from $m$ to $n$). This means that, *modulo* a renormalization of the density operator (which only amounts to a redefinition of the engine interaction $M_{mp}^{nq}$), the heat flow between two reservoirs with multiple levels (and thus multiple transitions) is formally equivalent to the flow between multiple reservoirs, each one with only two levels (and thus only one transition). A single engine working between the cold and the hot reservoirs is thus equivalent to a set of different engines, each one working between two reservoirs composed, respectively, of the two-level systems made of the levels $(p,q)$ and $(m,n)$.

This point is important for us because a two-level system with arbitrary level populations $\rho_0$ and $\rho_1$ and level energies $E_0$ and $E_1$ can always be considered in thermal equilibrium for a certain effective temperature $T_{\text{eff}}$. This is due to the elementary calculus result that, given two arbitrary points in the Cartesian plane, there is always an exponential function connecting them (see Fig. 2 for a schematic illustration). The

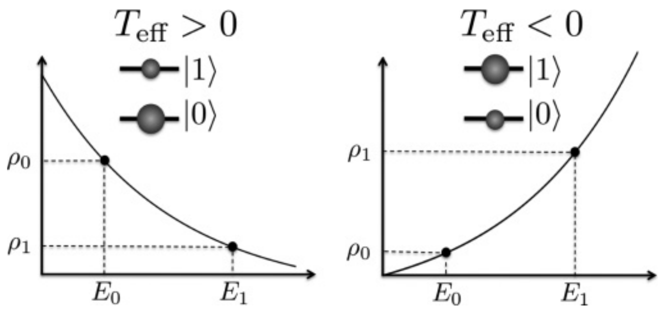


FIG. 2. An arbitrary two-level system, with level populations $\rho_0$ and $\rho_1$ and level energies $E_0$ and $E_1$, can always be considered in thermal equilibrium for a certain effective temperature $T_{\rm eff}$. This temperature is positive if the lower-lying level population is higher (left) and negative otherwise (right).

effective temperature $T_{\rm eff}$, which can be positive or negative, is thus given by the equation

$$\frac{\rho_1}{\rho_0} = e^{-(E_1-E_0)/T_{\rm eff}}. \tag{21}$$

From the two remarks above we obtain one of our main results: *An arbitrary time-independent reservoir is formally equivalent to a collection of equilibrium subreservoirs composed of two-level systems, each one characterized by its effective equilibrium temperature given by Eq.* (21).

Given that a reservoir is usually made up of many identical subsystems (e.g., the molecules of a gas), each transition will be highly degenerate. Through Eq. (21) this will give rise to many identical two-level systems, leading to subreservoirs roughly of the same size (in terms of the number of subsystems and thus of the number of available transitions) of the original ones. It is important to note that the equivalence is purely *formal*; these subreservoirs are only mathematical objects, useful abstractions. We are not suggesting that the reservoir is phisically divided into multiple pieces. It is also important to remember that the hypothesis that the initial states are stationary states of the decoupled reservoirs [Eq. (1)] is required for the theorem to hold.

## V. GENERALZED CARNOT'S THEOREM

From the theorem proven in the previous section, the generalization of Carnot's theorem we are looking for follows quite naturally. Being a nonthermal reservoir equivalent to a collection of equilibrium subreservoirs, an engine working between two of them is in fact formally equivalent to one operating between two sets of equilibrium subreservoirs, each one with its own effective temperature. The engine couples pairs of subreservoirs, one from the cold side and the other from the hot one, extracting work from them (see Fig. 3 for a schematic illustration in the case of two reservoirs composed of three-level systems). We now have a system that can be described using only thermal reservoirs and we can thus easily find an upper bound to its efficiency using the standard Carnot theorem and the tools we develop in Sec. III. Using Eq. (21)

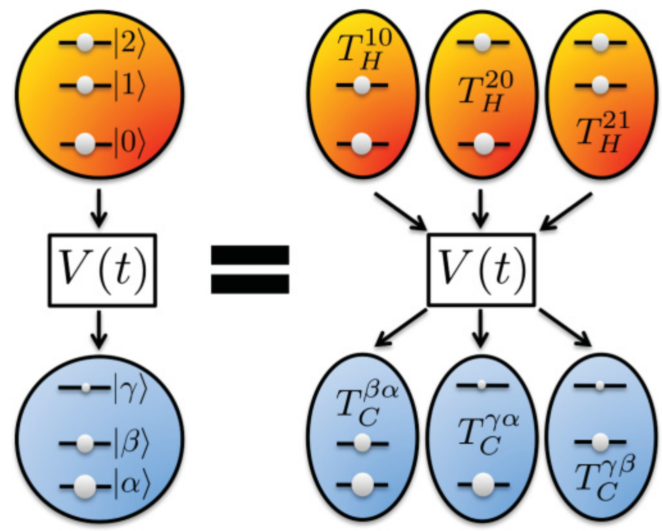


FIG. 3. (Color online) An engine working between two nonthermal reservoirs is formally equivalent to an engine working between two sets of thermal sub-reservoirs.

we can define the effective, transition-dependent temperatures for each pair of levels as

$$\begin{aligned} T_C^{qp} &= \left(E_C^q - E_C^p\right)/\log\frac{\rho_C^p}{\rho_C^q},\\ T_H^{mn} &= \left(E_H^m - E_H^n\right)/\log\frac{\rho_H^n}{\rho_H^m}, \end{aligned} \tag{22}$$

and, following the standard Carnot theorem or, better, its trivial expansion to the case of multiple reservoirs, we obtain the following upper bound on the efficiency of energy extraction from the nonthermal reservoirs:

$$\eta \leqslant 1 - \frac{\min\left(T_C^{qp}\right)}{\max\left(T_H^{mn}\right)}, \tag{23}$$

where the minimum and the maximum are taken, respectively, over all the pairs of levels in the cold $(p,q)$ and hot $(m,n)$ reservoirs.

In particular, the engine described by an operator $M_{mp}^{nq}$, whose only nonzero elements have indexes $(\tilde{m},\tilde{n})$ and $(\tilde{p},\tilde{q})$ that satisfy

$$T_H^{\tilde{m}\tilde{n}} = \max\left(T_H^{mn}\right), \quad T_C^{\tilde{q}\tilde{p}} = \min\left(T_C^{qp}\right), \tag{24}$$

couples only pairs of transitions corresponding to the lowest and highest temperature; that is, it works only between the coldest and the hottest reservoir. It will thus obey Eq. (23) and it can saturate the inequality if all the transitions take place between almost-equilibrium states, as explained in Sec. III.

In order to write Eq. (23) we made two supplementary hypotheses: all the effective temperatures are positive and all the effective temperatures of the hot reservoir are hotter than those of the cold one. If the first hypothesis is violated, it could be possible to construct an engine extracting work from a single reservoir; if the second is violated, we could extract work from bidirectional heat flows. In both cases, while our formalism is completely apt for studying them, the usual definition of efficiency is not well suited (see the discussion about work reservoirs in Sec. II) and thus it is meaningless to apply Carnot's theorem, and we thus ignore these possibilities. We have proved that the determination of the upper bound of the efficiency can be reduced to the calculation of the extrema of the effective temperatures in the two reservoirs.

While we consider in the following only examples concerning systems with discrete spectra, the same procedure can be generalized to the generic continuum case. The effective temperatures in each reservoir will then form two-dimensional surfaces and their extrema can be located by usual analytic or numerical methods.

## VI. APPLICATION TO A KNOWN CASE

In the final part of this paper, we apply the theory just developed to study the efficiency that can be obtained from reservoirs presenting some amount of quantum coherence. This case was treated in a paper by Scully and coworkers [2]. In this paper they showed how, given a reservoir consisting of a thermal gas of three-level atoms with a certain amount of quantum coherence between the quasidegenerate two lower levels, it is possible to build an engine with an efficiency greater than the one given by Carnot's theorem. In order to do that, they devised a photo-Carnot engine whose working fluid is composed of photons, which uses the thermal three-level quantum coherent atom gas as a hot reservoir and a generic reservoir at the same temperature, but without coherence, as a cold one. We show how our theory allows us to find the same results in a completely model-independent way (that is, without any need of devising an actual engine).

Following Ref. [2] we define a thermal, quantum coherent system as a system whose density matrix has diagonal elements given by thermal populations and some nonzero off-diagonal terms. The coherent gas is thus described by the density matrix

$$\rho_\phi = \begin{pmatrix} P_a & 0 & 0 \\ 0 & P_b & \rho_{bc}e^{i\phi} \\ 0 & \rho_{bc}e^{-i\phi} & P_c \end{pmatrix}, \tag{25}$$

where the diagonal elements are the thermal populations of the three states. In the following we consider the degenerate case $P_b = P_c$, in order to satisfy Eq. (1) and be able to apply our equivalence theorem, and we call $\Omega$ the energy gap between the higher level and the lower two. In the limit of high temperature and small coherence, Scully and coworkers find an efficiency for the photo-Carnot engine depending on the phase between the two coherent levels, given by

$$\eta_\phi = -\frac{P_a\rho_{bc}\cos(\phi)}{P_b(P_b - P_a)}, \tag{26}$$

where, given the two reservoirs at the same temperature, we would expect a zero efficiency in the absence of coherence. To apply our theory we diagonalize the density matrix in Eq. (25), obtaining the eigenvalues $[P_a, P_b - \rho_{bc}, P_b + \rho_{bc}]$. The thermal, coherent gas, is thus equivalent to a fully incoherent, but nonthermal gas. Applying Eq. (22), we find the following three effective temperatures for the hot reservoir,

$$\begin{aligned} T_H^{ab} &= \Omega/\log\left(\frac{P_b - \rho_{bc}}{P_a}\right), \\ T_H^{ac} &= \Omega/\log\left(\frac{P_b + \rho_{bc}}{P_a}\right), \\ T_H^{bc} &= 0, \end{aligned} \tag{27}$$

while for the incoherent, cold reservoir, we have a single, equilibrium temperature,

$$T_C = \Omega/\log\left(\frac{P_b}{P_a}\right). \tag{28}$$

Substituting Eqs. (27) and (28) into Eq. (23), we obtain the maximal efficiency given by

$$\eta \leqslant 1 - \frac{\log\left(\frac{P_b - \rho_{bc}}{P_a}\right)}{\log\left(\frac{P_b}{P_a}\right)}, \tag{29}$$

which, in the high-temperature ($P_b \simeq P_a$) and small-coherence ($\rho_{bc} \ll 1$) regime, reduces to

$$\eta \leqslant \frac{P_a\rho_{bc}}{P_b(P_b - P_a)}, \tag{30}$$

that is, the maximum of Eq. (26) [actually, following the calculations in Ref. [2], but without making any simplifying approximation, we would find the optimal efficiency exactly as in Eq. (29)]. We have thus proved that our theory can correctly predict, in a model-independent way, the maximal efficiency of the photo-Carnot engine. Moreover, we have shown that the efficiency found in Ref. [2] is indeed optimal for the chosen cold and hot reservoirs.

## VII. UNIT EFFICIENCY ENGINE

While proving the results in the previous section, we stumbled on a rather unexpected result. One of the temperatures in Eq. (27), corresponding to the transition between the two coherent degenerate levels, is equal to 0. This seems to imply that, switching the two reservoirs, that is, using the coherent reservoir as the cold one, it should be possible to conceive an engine working at unit efficiency [the $T_C$ in Eq. (23) is equal to 0 and thus $\eta = 1$].

Initially puzzling, this turns out to be a generic feature of reservoirs with degenerate, coherent levels. Two coherent degenerate levels are generally described by a density matrix of the form

$$\rho_c = \frac{1}{2}\begin{pmatrix} 1 & \sigma \\ \sigma & 1 \end{pmatrix}, \tag{31}$$

which, after diagonalization, yields an effective zero temperature, as can be seen from Eq. (22), because the energies are equal while the populations are different.

The physical origin of such seemingly unphysical behavior is easy to understand. The entropy of $\rho_c$ is always lower than that of the fully incoherent density matrix

$$\rho_i = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{32}$$

Since all the states in such a degenerate subspace have the same energy, the reservoir can act as a perfect entropy drain, absorbing entropy but not energy from the engine as it evolves from $\rho_c$ to $\rho_i$. We thus predict the possibility of realizing an engine with unit efficiency, extracting work from a single reservoir and dissipating entropy by destroying coherence in a second, coherent reservoir. The maximal efficiency of such an engine would be independent of the strength of the coherence $\sigma$, but the work extractable from it would depend on the total amount of coherence that is burned by the engine. A simple application of the second law of thermodynamics gives the upper bound

$$W \leqslant T_H M \Delta S, \tag{33}$$

where $M$ is the total number of pairs of levels whose coherence is utilized to extract work $W$ and $\Delta S$ is the entropy difference between $\rho_i$ and $\rho_c$. While such predictions of high efficiencies might seem to violate the usual Carnot bound, this is not the case. In fact, as stated above, we are considering the efficiency of work extraction from reservoirs already in a nonthermal state. In order to compare these results with the ones obtained for thermal reservoirs, we should also consider the processes needed to bring the reservoirs out of thermal equilibrium in the first place. Illuminating discussions in the case of the photo-Carnot engine can be found in Refs. [7] and [8].

The above construction is rather formal, but there are simple and well-known systems that implement the mechanism described. Without entering into detailed calculations, which are beyond the scope of this paper, we can note that a laser without inversion [9] driven by a thermal field can indeed behave as a unit efficiency engine. If the active medium is composed of coherent, degenerate $\Lambda$ atoms, whose upper level is at an energy high enough to be able to neglect its thermal occupation, such a system effectively extracts energy (in the form of laser radiation) from the thermal reservoir (the thermal field) with unit efficiency, while destroying the coherence of the $\Lambda$ atoms.

It is also interesting to note that destroying coherence between degenerate levels is not the only way to eliminate entropy without losing energy. A number of investigations have indeed shown, exploiting the links between thermodynamics and information theory [10–16], that if information is somehow extracted from the system, it is possible to obtain an engine working at unit efficiency.

## VIII. CONCLUSIONS AND PERSPECTIVES

In the present paper we have introduced a new approach to study of the efficiency of thermal engines that allows us to treat general nonthermal and quantum coherent reservoirs. We have proved that our approach gives the same result as the canonical one when applied to thermal situations (Sec. III) and yields the right result when applied to the only case of a nonthermal reservoir thoroughly studied in the literature (Sec. V). While the formalism we developed differs in many respects from what is usually done in standard thermodynamics, the fact that it is able to give the right results in all known situations vindicates the correctness of our approach.

As applications we reproduced the results originally derived in Ref. [2] and then showed the possibility of realizing an engine with unit efficiency that exploits quantum coherence.

The aforementioned results were derived using rather formal methods. It will be an interesting challenge to identify and study physical systems in which such results can be tested and applied.

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## APPENDIX: PROOF OF EQUATION (14)

In Sec. III we claimed that, in order to have an engine that extracts heat from the hot reservoir, we need to have

$$\rho_H^m \rho_C^p - \rho_H^n \rho_C^q > 0, \tag{A1}$$

at least for some value of the indexes $(m,n,p,q)$. Here we give a detailed justification of this point.

Following what is done in Sec. III we can write the heat fluxes from the two reservoirs as

$$\begin{aligned} Q_C &= \lambda^2 \sum_{\substack{m,n,p,q \\ E_H^m > E_H^n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_C^p - E_C^q\right), \\ Q_H &= \lambda^2 \sum_{\substack{m,n,p,q \\ E_H^m > E_H^n}} \left|M_{mp}^{nq}\right|^2 \left(\rho_H^m \rho_C^p - \rho_H^n \rho_C^q\right)\left(E_H^m - E_H^n\right), \end{aligned} \tag{A2}$$

and we assume the reservoirs to be thermal,

$$\rho_H^m = e^{-E_H^m/T_H}/Z_H, \quad \rho_C^p = e^{-E_C^p/T_C}/Z_C, \tag{A3}$$

with $T_H > T_C$. The explicit form we derived for $Q_C$ and $Q_H$ in Eq. (A2) allows us to write the heat fluxes between the reservoirs and the engine as a sum over different channels, indexed by the 4-tuple $(m,n,p,q)$. If we examine the contribution of each channel to $Q_C$ and $Q_H$, we realize that, in order for the channel to extract some heat from the reservoirs, we need two conditions to be fulfilled:

(1) at least one of the two contributions has to be positive; and

(2) if only one contribution is positive, its norm has to be bigger than the norm of the other.

If these two conditions are not fulfilled, the channel is effectively dissipating work into the reservoirs and, thus, lowering the overall efficiency. In order to have an engine extracting some work, we thus need these two conditions to be fulfilled at least for some channel.

In the rest of this Appendix we prove that any channel fulfilling the two conditions has $Q_H > 0$ and $Q_C < 0$, and thus it verifies Eq. (A1). We prove this by showing that any other possibility leads to contradiction.

#### 1. $Q_H > 0$ and $Q_C > 0$

Having both contributions from Eq. (A2) positive would imply

$$\rho_H^m \rho_C^p - \rho_H^n \rho_C^q > 0 \tag{A4}$$

and

$$E_C^p - E_C^q > 0. \tag{A5}$$

Yet, using the reservoirs in Eq. (A3), Eq. (A4) implies

$$\frac{E_C^q - E_C^p}{E_H^m - E_H^n} > \frac{T_C}{T_H}, \tag{A6}$$

which is never verified, as the left-hand side is negative. We have thus proved that it is not possible for an engine to extract heat from both reservoirs.

#### 2. $Q_H < 0$ and $Q_C > 0$

This would imply, from Eq. (A2),

$$\rho_H^m \rho_C^p - \rho_H^n \rho_C^q < 0. \tag{A7}$$

Condition (2) thus imposes the following inequality:

$$E_C^q - E_C^p > E_H^m - E_H^n. \tag{A8}$$

From Eqs. (A7) and (A8), using the reservoirs in Eq. (A3), we obtain the relation

$$1 < \frac{E_C^q - E_C^p}{E_H^m - E_H^n} < \frac{T_C}{T_H}, \tag{A9}$$

which is also never verified. We have thus proved that it is not possible for an engine to work by extracting heat from the cold reservoir.

#### 3. $Q_H < 0$ and $Q_C < 0$

This case would trivially violate condition (1), as both contributions are negative.


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