



Limitations on the Evolution of Quantum Coherences: Towards Fully Quantum Second Laws of Thermodynamics

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(Received 17 February 2015; revised manuscript received 29 September 2015; published 18 November 2015)

The second law of thermodynamics places a limitation into which states a system can evolve into. For systems in contact with a heat bath, it can be combined with the law of energy conservation, and it says that a system can only evolve into another if the free energy goes down. Recently, it's been shown that there are actually many second laws, and that it is only for large macroscopic systems that they all become equivalent to the ordinary one. These additional second laws also hold for quantum systems, and are, in fact, often more relevant in this regime. They place a restriction on how the probabilities of energy levels can evolve. Here, we consider additional restrictions on how the coherences between energy levels can evolve. Coherences can only go down, and we provide a set of restrictions which limit the extent to which they can be maintained. We find that coherences over energy levels must decay at rates that are suitably adapted to the transition rates between energy levels. We show that the limitations are matched in the case of a single qubit, in which case we obtain the full characterization of state-to-state transformations. For higher dimensions, we conjecture that more severe constraints exist. We also introduce a new class of thermodynamical operations which allow for greater manipulation of coherences and study its power with respect to a class of operations known as thermal operations.

DOI: [10.1103/PhysRevLett.115.210403](https://doi.org/10.1103/PhysRevLett.115.210403)

PACS numbers: 05.30.-d, 03.65.Ta, 03.67.-a, 05.70.Ln

We consider a quantum system in state ρ_S which can be put in contact with a reservoir at temperature T . The second law of thermodynamics, combined with the first law (conservation of energy) states that the free energy

$$F = \text{Tr}(H\rho_S) - TS(\rho_S) \quad (1)$$

can only decrease, where $S(\rho_S)$ is the von Neumann entropy (one can also take the course grained entropy, but since we are interested in small quantum systems where all degrees of freedom can be precisely measured, in principle, taking the von Neumann entropy will help us answer the questions we are interested in here.) $S(\rho) = -\text{Tr}\rho \log \rho$ and H is the system's Hamiltonian. Although this is a necessary constraint on what state transformations are possible, we now know that it is not sufficient. For transitions between two states, diagonal in the energy basis, there are a set of necessary and sufficient conditions which must be satisfied in order for a state to transform into another state. One has a family of free energies in the case of catalytic processes [1] (i.e., where one is allowed an ancilla which can be returned to its original state in the spirit of the Clausius-Planck formulation of the second law). For noncatalytic transformations, the set of necessary and sufficient conditions were proven to be majorization [2] in the case when the Hamiltonian is $H = 0$ and thermomajorization [3] in general. It is only in the thermodynamic limit

that all these conditions become equivalent to the ordinary second law of Eq. (1). However, for single finite systems (sometimes called the single-shot scenario), the full set of conditions is relevant. It is this finite regime which is more relevant for quantum systems or even in the mesoscopic regime, especially if long range interactions are present.

Regarding states that are not diagonal in the energy basis, thermomajorization (or the generalized free energies of Ref. [1] in the catalytic case) are still necessary conditions for state transformations and place conditions on the diagonal entries of the state ρ_S (where we assume that ρ_S is written in the energy eigenbasis). But these conditions do not say anything about how off-diagonal elements between different energies behave. Partial results were obtained in Refs. [1,3] for the case where only the input state is nondiagonal and simultaneously posted with this Letter, in Ref. [4], where relations between purity and quantum asymmetry in the spirit of coherences have been formulated and the authors obtained the “free-energy relation” for coherences (second law). However, finding a complete set of quantum limitations is still a challenge. Here, by providing a first systematic approach to coherences, we will present a set of conditions, called damping matrix positivity (DMP). Unlike the results of Refs. [1,3], they are not necessary and sufficient, although we will show that they are for the case of a qubit.

Since we are interested in studying fundamental limitations, we allow for the experimenter to perform the largest possible set of operations within the context of thermodynamics. Namely, we allow them to have access to a heat bath at temperature T , and to perform any unitary. Since the laws of physics must conserve energy, and we are interested in how energy flows in thermodynamics, the unitary should conserve the total energy of all systems it acts on, but this is the only restriction. This provides a precise definition of what we mean by thermodynamics, recasting it as a resource theory known as thermal operations (TO). This was introduced in Ref. [5] (cf. Ref. [6]) and applied later in Refs. [3,7], where the addition of a work system enabled one to compute the work required for a state transformation. We will define these operations more carefully and then derive the restrictions they impose on state transformations. In particular, we will present our conditions, and discuss it in detail for qubits, where we see that DMP is a necessary and sufficient condition for state transformations. As a result, we fully characterize the qubit-qubit case, as well as provide limitations for higher dimensional states. Then, we introduce a new class of operations we call enhanced thermal operations, and study its power with respect to TO. They appear to be more powerful, in that for them, DMP are necessary and sufficient conditions for state transformations, while for TO we believe DMP are not sufficient. At least in the qubit case, TO can be described by three conditions: completely positive trace preserving, some commutation relation, and preservation of the Gibbs state. We obtain a part of our findings by adapting results for studies of the weak coupling between the system and the heat bath, and dynamical semi groups [6,8–10].

Thermodynamics as a resource theory and thermal operations.—In order to derive any laws of thermodynamics we need to say what thermodynamics is—in other words, define the class of operations which constitute thermodynamics. Thermodynamics is then viewed as a resource theory [2,3,5,7,11]. In the resource theory, one considers some class of operations, and then asks how much of some resource can be used to perform the desired task and how this resource can be manipulated. In the case of thermodynamics, it is viewed as a theory involving state transformations in the presence of a thermal bath. To describe it, one can then exploit some mathematical machinery from single-shot information theory, where one does not have access to many copies of independent and identically distributed bits of information [12].

We wish to explore fundamental limitations on state transformations; therefore, we should allow the experimenter to perform any unitary transformation. However, any interaction allowed in nature has to conserve energy if we consider the total system, and since thermodynamics requires precise accounting of all sources of energy, the unitary must conserve energy. Of course, we often consider adding interaction Hamiltonians, or performing unitaries

which do not conserve energy, but this is only because we are ignoring degrees of freedom which, if their change in energy was taken into account, would restore energy conservation. Here, we need to include these additional systems, not only because we want to account for all sources of energy, but because we want to understand coherences and these additional systems may contain coherences which could be transferred to our system. We thus consider all systems with coherence as being part of the system. Indeed all the standard thermodynamical paradigms we are interested in can be made to fall within thermodynamics in this manner [7]. We can thus use thermal operations (TO) to study fundamental limitations on the manipulation of coherences. The TO paradigm preassumes that there is a heat bath, described by a Gibbs state and helps to describe what can happen with a system which can interact with the heat bath. It also treats the microscopic system, without any approximations.

Formally, under TO one can (i) bring in an arbitrary system in a Gibbs state with temperature T (free resource), (ii) remove (discard) any system, and (iii) apply a unitary that commutes with the total Hamiltonian.

The class of TO is generated by the unitaries U (which act on the system, bath, and other ancillas), which obey the energy conservation condition

$$[U, H_S + H_R + H_W] = 0, \quad (2)$$

where H_W is a work system or a clock, or any other object under consideration besides the system and bath. Equation (2) is necessary and sufficient if we wish to ensure that energy is conserved on every input state [3]. This is natural if we wish to apply our thermal machine on arbitrary unknown quantum states. Thus, an arbitrary thermal operation is obtained by the implementation of an energy-preserving U and tracing out the heat bath (see also, Fig. 1). Precisely, $\Lambda \in \text{TO}$, when

$$\Lambda(\rho_S) = \text{Tr}_R(U\tau_R \otimes \rho_S U^\dagger). \quad (3)$$

It is worth noting that it is Eq. (2) that prevents one from creating coherences over energy levels if one doesn't already start with them. One can extend TO to the case where one is allowed as a resource, a reference frame which acts as a source of infinite coherence, and, in such a case, one can lift the superselection imposed by Eq. (2) (in the context of thermodynamics, see Refs. [7,13]).

Allowed state-to-state transformations under thermal operations.—As we already mentioned, TO cannot create coherent superpositions between eigenstates; but what are the ultimate limitations for a general $(\rho, H_S) \rightarrow (\sigma, H_S)$ state-to-state transition? In Ref. [3] necessary and sufficient conditions, in terms of monotones, have been put forward for the block diagonal entries of a state written in the energy basis. These conditions are discussed in the Supplemental

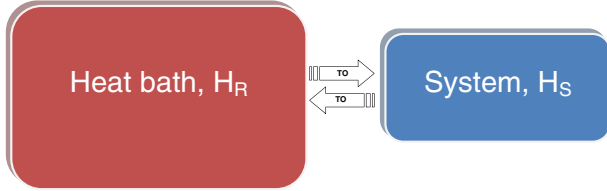


FIG. 1 (color online). One considers a system S in a quantum state ρ_S with a fixed Hamiltonian H_S , in contact with the thermal reservoir (heat bath) R in a Gibbs state τ_R (possibly many copies of it) with Hamiltonian H_R —acting as a free resource. Interactions (white arrows) between them are implemented under the paradigm of thermal operations (TO), i.e., by energy preserving, unitary operations U , commuting with the total Hamiltonian. The goal is to obtain some other state σ_S . The energy spectrum of the bath is highly degenerated (small or no degeneracy drastically reduce the set of thermal operations) and its maximal energy will tend to infinity. We also make an assumption that the dimension of the bath is much larger than that of the system. Moreover, initially, the total system is in the product state of the bath and system $\tau_R \otimes \rho_S$.

Material, note 4 [14]. Here, by noticing some general properties of TO, we will provide bounds for off-diagonal elements—*coherences*, under the assumption that the system Hamiltonian H_S has a nondegenerate Bohr spectrum; i.e., there are no degeneracies in the nonzero differences of energy levels of the Hamiltonian. To obtain some of our results, we will adapt results derived for open systems, precisely, for Davies maps under weak coupling [8–10].

Properties of thermal operations.—Let us examine the properties of TO. First, the diagonal elements of a density matrix are not mixed with off-diagonal ones during evolution under TO (i.e., they evolve independently). Moreover, for systems having nondegenerated Bohr spectra, coherences are not mixed among themselves. We can thus say that TO are block diagonal; i.e., for an off-diagonal (diagonal) element $|i\rangle_S\langle j|$ ($|i\rangle_S\langle i|$) of state ρ_S one gets (for proofs, see, the Supplemental Material, note 2 [14])

$$\Lambda(|i\rangle_S\langle j|) = \alpha_{ij}|i\rangle_S\langle j|, \quad i \neq j \quad (4)$$

and

$$\Lambda(|i\rangle_S\langle i|) = \sum_{ij} p(i \rightarrow j)|j\rangle_S\langle j|, \quad (5)$$

where Λ is defined as in Eq. (3), α_{ij} are factors by which the off-diagonal elements are multiplied (damped) during the transition, and $p(i \rightarrow j)$ is a transition probability of moving element i into j , and $p(i)$ is a probability of occupying an energy state i .

TO are physical operations, so the dynamics should be implemented by completely positive trace preserving maps (CPTP maps). Together with the fact that under TO, the

Gibbs state is preserved, we have a set of properties fulfilled by TO. It is known [8,9] that these properties are also satisfied by Davies maps appearing in the weak-coupling regime for Hamiltonians with nondegenerate Bohr spectra. Using the above properties, we obtain constraints for the behavior of coherences. We thus get bounds for off-diagonal elements that are determined by the probability for staying in the same energy level.

Quantum states—second laws for off-diagonal elements.—We will now use the above properties of TO to study allowed states transitions. From the property given by Eqs. (4)–(5), we obtain that there exist two families of bounds, one for diagonal elements of states (thermomajorization) and the second one for coherences.

Suppose now that somehow we can transform the diagonal of an input d -level state into another d -level state with some other diagonal entries. Our main question is then, how does this process affect coherences, i.e., the off-diagonal elements?

To answer, let us use other properties of TO. As shown in Ref. [8], the property of CPTP combined with formulas (4) and (5) imply that the following matrix must be positive:

$$\begin{bmatrix} p(0 \rightarrow 0) & \alpha_{01} & \dots & \alpha_{0n-1} \\ \alpha_{10} & p(1 \rightarrow 1) & \dots & \alpha_{1n-1} \\ \vdots & \vdots & \ddots & \vdots \\ \alpha_{n-10} & \alpha_{n-12} & \dots & p(n-1 \rightarrow n-1) \end{bmatrix} \geq 0. \quad (6)$$

We will call the above matrix the damping matrix, and the above condition, damping matrix positivity (DMP). Let us note that the matrix is crucial for processing coherences. Indeed, positivity implies that the damping factors, in particular, satisfy

$$|\alpha_{ij}| \leq \sqrt{p(i \rightarrow i)p(j \rightarrow j)}. \quad (7)$$

Thus, the coherences must be damped at least by a factor $\sqrt{p(i \rightarrow i)p(j \rightarrow j)}$ that comes from the 2×2 minors of the matrix from Eq. (6). Since the present Letter first appeared, the formulas has been generalized to the case of an arbitrary spectrum in Ref. [15]. In the subsequent section we will show that for qubits, this is the only constraint for processing coherences by TO.

Qubit example.—For qubits, we have necessary and sufficient sets of criteria, by showing that for a given process on a diagonal, the damping factor (for coherences) from Eq. (7) can always be equal to $\sqrt{p(i \rightarrow i)p(j \rightarrow j)}$. We will determine this optimal factor for an arbitrary $\rho \rightarrow \sigma$ transition.

Going into detail, consider two states $\rho_S = \begin{bmatrix} p & \alpha \\ \alpha^* & 1-p \end{bmatrix}$ and $\sigma_S = \begin{bmatrix} q & \chi \\ \chi^* & 1-q \end{bmatrix}$, written in the energy eigenbasis of

the Hamiltonian system H_S , where $*$ stands for complex conjugation. We know that the evolution of diagonal elements can be separated from off-diagonal ones, so the former one uses thermomajorization (leading to four different situations discussed in the Supplemental Material, note 3 [14]). For the latter, we obtain that the decaying rate of coherences depends only on the diagonal transition rates (and, consequently, on elements of states and energies associated with the Hamiltonian of the system). Namely, coherences obey the following inequality:

$$|\chi| \leq |\alpha|\kappa, \quad (8)$$

where

$$\kappa = \frac{\sqrt{(q - \tilde{p}e^{\beta\Delta E})(p - \tilde{q}e^{\beta\Delta E})}}{|p - \tilde{p}e^{\beta\Delta E}|}, \quad (9)$$

$\tilde{q} = 1 - q$, $\tilde{p} = 1 - p$, $e^{\pm\beta\Delta E} = e^{\pm\beta(E_j - E_i)}$, with E_i being the energy of the system and $\beta = 1/kT$ the inverse temperature. Note that the phases commute with the total Hamiltonian of our setup, so we can restrict our attention only to moduli of the coherences. We have necessary and sufficient conditions for arbitrary qubit $\rho \rightarrow \sigma$ transitions under TO, where for (a) diagonal elements we use thermomajorization, (b) for coherences, Eq. (8) (in the Supplemental Material, note 4 [14] we show that it can be achieved with equality). In the Appendix, we also express our damping factor in terms of relaxation times (T_2) [16,17].

Sufficiency of the second laws?—It is clear that for an arbitrary transitions, there are many stochastic maps that lead to the same final state and each such map can be implemented by possibly many unitary transformations. We need such unitaries that damp as little as possible, the off-diagonal elements of the density matrix—for which, the inequalities coming from the 2×2 minors of the Choi map from Eq. (7) are all saturated. This would optimize the preservation of coherences. But, is it always possible? As we have shown, for qubits, for every state-to-state transition, we have only one channel that realizes it and we can always make the inequality that gives us a damping factor for coherences tight. This uniqueness of channel may not be true anymore for higher dimensional states. In the Supplemental Material, note 6 [14], we choose a qutrit state-to-state transition $(0, \frac{1}{2}, \frac{1}{2}) \rightarrow \{(e^{-\beta\Delta E_{21}}/2), [(1 - e^{-\beta\Delta E_{21}} + e^{-\beta\Delta E_{20}})/2], [(1 - e^{-\beta\Delta E_{20}})/2]\}$, which can only be realized by a unique set of transition probabilities. For this set of transition probabilities, one is not able to find a unitary map that at the same time realizes the exact states transition and leads to the saturation of bounds for coherence preservation.

Enhanced thermal operations: a class of operations which saturate the DMP criteria.—As we already have observed, in the case when one considers Hamiltonians

with nondegenerated Bohr spectra, the properties of TO used in this Letter are similar to those occurring when one studies Davies maps for many-level systems. We shall now introduce a class of operations that is defined by these properties. We will call this class enhanced thermal operations.

We define enhanced thermal operations (ETO) in the following way. $\Lambda \in \text{ETO}$ when (i) $[\Lambda, \hat{H}_S] = 0$, (ii) it is CPTP, and (iii) it preserves the Gibbs state.

Here, \hat{H}_S is a superoperator defined by $\hat{H}_S(X) = [H_S, X]$ for all operators X . The first property gives us that under ETO, one is able to realize all possible transformations that satisfy the constraints given by Eq. (6). We will use our previous findings to compare the power of these two classes.

We show that for qubits, TO are equal to the new class and as a result we have laws for any state-to-state transition under TO. Essentially, for qubits, TO can already saturate the bound given by Eq. (6) and thus do no worse than enhanced thermal operations. For qutrits, we provided a family of initial and final states ρ and σ that by enhanced thermal operations, one can transform ρ into σ exactly, but it is not possible under TO. Based on this, one can try to conclude that TO are outperformed by enhanced thermal operations, and, what is more, state transitions by TO are not equal to the ones under enhanced thermal operations (the latter statement is stronger, it could be that the set of TO is smaller than enhanced thermal operations, but both classes lead to the same laws of transformations). However, it is not a conclusive result, because one can try to approximate the channel that is used to realize the transition under TO from the previous section, which may lead to the

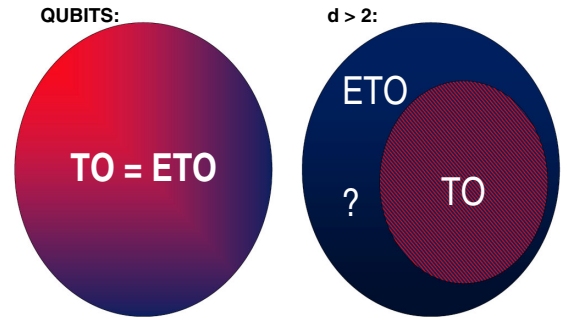


FIG. 2 (color online). Comparison of thermal operations and enhanced thermal operations for qubits ($d = 2$) (a) and $d > 2$ (b). For $d = 2$, they are equivalent, and from the Birkhoff primitive given in Ref. [7] TO can reproduce not only the extreme maps (when our bounds are saturated) but any other from ETO with an arbitrary precision. On the other hand, when $d > 2$, ETO may be a wider class than thermal operations. However, we only have a counterexample for an exact qutrit state-to-state transition, where we find a transition that can be realized by ETO, but not by TO. Studies of approximate states transitions are needed to verify the possible gap between TO and ETO.

saturation of the bound for optimal coherences preservation; see also Fig. 2.

Discussion and open questions.—We study the limit of state-to-state transformations under thermal operations, focusing mostly on coherences and their preservation. We also introduce a new class of operations—enhanced thermal operations, and compared its power to TO. A natural research direction is to study whether they really outperform thermal operations if we are only concerned about approximate transformations.

It would also be interesting to check how state transitions look if we add additional ancillas, and allow them to be returned in approximately the same state as before. Such catalytic thermal operations were studied in Ref. [1] and depending on the level of approximation, they effectively allow one to only approximately conserve energy on the system.

Finally, we have seen that the second laws we have introduced in the form of the DMP criteria are not strictly necessary and sufficient limitations on thermodynamical transformations. This likely means that there are more second laws which have to be satisfied. Finding them is an interesting open question.

We want to thank David Reeb for useful discussions. We would also like to thank Anna Studzińska for preparing some of the figures. J. O. is supported by the Royal Society. M. S. and P. Ć. are supported by Grant No. 2012/07/N/ST2/02873 from National Science Centre. M. H. and P. Ć are also supported by the Seventh framework programme Grant RAQUEL No. 323970. M. H. is also supported by the NCN Grant Maestro DEC-2011/02/A/ST2/00305. Research was (partially) completed while J. O., M. S. and P. Ć. were visiting the Institute for Mathematical Sciences, National University of Singapore, and (by all authors) during the program “Mathematical Challenges in Quantum Information” at the Isaac Newton Institute for Mathematical Sciences at the University of Cambridge. Part of this work was done at the National Quantum Information Centre of Gdańsk.

- [1] F. G. S. L. Brandao, M. Horodecki, N. H. Y. Ng, J. Oppenheim, and S. Wehner, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 3275 (2015).
- [2] M. Horodecki, P. Horodecki, and J. Oppenheim, *Phys. Rev. A* **67**, 062104 (2003).
- [3] M. Horodecki and J. Oppenheim, *Nat. Commun.* **4**, 2059 (2013).
- [4] M. Lostaglio, D. Jennings, and T. Rudolph, *Nat. Commun.* **6**, 6383 (2015).
- [5] D. Janzing, P. Wocjan, R. Zeier, R. Geiss, and T. Beth, *Int. J. Theor. Phys.* **39**, 2717 (2000).
- [6] R. F. Streater, *Statistical Dynamics: A Stochastic Approach to Nonequilibrium Thermodynamics* (Imperial College Press, London, 1995), ISBN 1848162502.
- [7] F. G. S. L. Brandão, M. Horodecki, J. Oppenheim, J. M. Renes, and R. W. Spekkens, *Phys. Rev. Lett.* **111**, 250404 (2013).
- [8] W. Roga, M. Fannes, and K. Życzkowski, *Rep. Math. Phys.* **66**, 311 (2010).
- [9] R. Alicki and L. Lendi, *Quantum Dynamical Semigroups and Applications*, 2nd ed. (Springer, New York, 2008).
- [10] R. Alicki, *Rep. Math. Phys.* **10**, 249 (1976).
- [11] G. Gour, M. P. Müller, V. Narasimhachar, R. W. Spekkens, and N. Y. Halpern, *Phys. Rep.* **583**, 1 (2015).
- [12] R. Renner, Ph.D. thesis, ETH, Zurich, 2005.
- [13] J. Åberg, *Phys. Rev. Lett.* **113**, 150402 (2014).
- [14] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.115.210403> for the review of the formalism and properties of thermal operations and proofs of statements from the Letter with the special focus on energy preserving unitaries that are optimal for coherences evolutions, which includes Refs. [18–21].
- [15] M. Lostaglio, K. Korzekwa, D. Jennings, and T. Rudolph, *Phys. Rev. X* **5**, 021001 (2015).
- [16] V. Gorini, A. Frigerio, M. Verri, A. Kossakowski, and E. Sudarshan, *Rep. Math. Phys.* **13**, 149 (1978).
- [17] G. Kimura, *Phys. Rev. A* **66**, 062113 (2002).
- [18] L. Masanes and J. Oppenheim, [arXiv:1412.3828](https://arxiv.org/abs/1412.3828).
- [19] M. Mitzenmacher and E. Upfal, *Probability and Computing: Randomized Algorithms and Probabilistic Analysis* (Cambridge University Press, New York, NY, USA, 2005), ISBN 0521835402.
- [20] J. von Neumann, *Tomck. Univ. Rev.* **1**, 286 (1937).
- [21] K. Fan, *Proc. Natl. Acad. Sci. U.S.A.* **37**, 760 (1951).