The Second Laws for Quantum and Nano-scale Heat Engines

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The second law in thermodynamics dictates which state transformations are statistically unlikely or effectively forbidden. However, the statistical formulation of the second law assumes the asymptotic regime, where a system of an asymptotically large number of particles interacts with the thermal baths. In addition, standard thermodynamics relies on mean values of thermodynamical quantities and admits thus the possibility of repeated measurements. This formulation cannot be automatically extended to the finite-size regime, where the system is composed of a small number of particles, let alone that these particles could be of quantum nature and that only one-shot measurement is allowed. In this work, we consider heat engines operating in the finite-size regime and allowed to access one-shot measurements, i.e., the engines are made up of a system with a finite or a small number of quantum particles and two baths at different temperatures, and convert heat into work. We introduce generalized engine operations, the semi-local thermal operations, where the system simultaneously interacts with two baths at different temperatures. We develop a resource theoretic formalism and show that, unlike in the asymptotic regime, thermodynamics of these quantum heat engines is fundamentally irreversible, and it requires many second laws to characterize the state transformations. We construct heat engines that operate with a one-step cycle. These engines improve the one-shot engine efficiency, compared to the engines operating with local thermal operations. Also, they can operate by exclusively exploiting the correlations present in the system. We formulate the statements of various forms of second laws such as one-shot Clausius, Kelvin-Planck, and Carnot statements in the finite-size regime.

I. INTRODUCTION

Heat engines are the fundamental building blocks of modern technology. These were invented primarily to convert heat into mechanical work. To lay a theoretical framework and to uncover the laws governing the processes in the engines, the thermodynamics was empirically developed. Later, it has been founded on statistical mechanics. There, the zeroth law establishes the notion of thermodynamical equilibrium. The first law ensures the total energy conservation for feasible thermodynamical processes, and thereby restricts the class of processes that are physically allowed. The second law provides the necessary and sufficient conditions for the transformations under such processes. For example, the Clausius statement of the second law says heat can never spontaneously flow from a colder to a hotter body in a heat engine. The laws find deep implications in the fundamental understanding of nature and are applicable in the domain beyond thermodynamics, such as quantum mechanics, relativivity, physics of black-holes, etc.

The formulation of standard thermodynamics (STh) based on statistical mechanics assumes that the systems are large and are composed of an asymptotically large number of particles \( N \to \infty \) interacting with even larger baths. This is termed usually as asymptotic regime. When we perform measurement of thermodynamical quantities we typically get answers corresponding to ensemble mean values. The ergodic theorem is assumed to be valid: time averages are actually equal to the ensemble averages. Therefore, the asymptotic regime is also assumed to allow many simultaneous or repeated measurements on the particles. Fluctuations are relatively small and “normal” - fluctuations of extensive quantities (proportional to the number of particles \( N \)) scale as \( \sqrt{N} \). If we restrict our interest to mean values of thermodynamic quantities in or off equilibrium only, then repeated measurements in time or simultaneous measurements on different particles of the system are equivalent. In contrast, if we are interested in fluctuations, in particular, non-equilibrium ones obtained in one-shot measurements, then even for large systems the prediction on such measurements requires careful analysis. There has been considerable efforts to describe and bound fluctuations in the out-of-equilibrium situation using the methods of statistical physics – these approaches led to derivation of various fluctuation theorems [1–3].

The situation changes completely for the systems of a finite, but moderate or even small number of particles \( N \ll \infty \). In such situations, from the very beginning, the fluctuations may play a much more important role. Therefore, one has to distinguish here two situations: Situation-1 – when we have access to a system with moderate or a small number of particles, and repeated measurements in time are allowed; we term this situation repeated-measurements finite-size regime. Alternatively, we may face the Situation-2 – when we restrict ourselves to one-shot measurements on a system composed of a single or a moderate number of particles. We term the Situation-2 as the one-shot finite-size regime. Note, for the cases that do not involve time evolution in the system, both the situations become identical.

In the last decades, enormous efforts have been put forward to extend thermodynamics to the regimes where a system is made up of a finite (typically moderate or small) number of quantum particles interacts with a single thermal bath, and has access to repeated, simultaneous, and one-shot measurements on the particles [4, 5]. These efforts lead to two major approaches to studying quantum thermodynamics.

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The first, which applies in fact to both asymptotic regime and repeated-measurements finite-size regime (Situation-1), is based on fluctuation theorems (FT), exploiting statistical mechanics and open quantum systems dynamics [1–3]. The other one is based on the quantum information theory [6–15]. The latter leads to a resource theory of quantum systems out of thermal equilibrium, i.e., resource theory of quantum thermodynamics (RTQTh) [6, 8, 10]. This is applicable to asymptotic regime, and both repeated-measurements and one-shot finite-size regimes (Situation-1 and Situation-2). The approaches can be classified in terms of their applications in different regimes, as given in the Table I.

| Regimes                  | Asymptotic \((N \to \infty)\) | Finite-size \((N \ll \infty)\) |
|--------------------------|-------------------------------|-------------------------------|
| Repeated measurements    | STh, FT, RTQTh                | FT, RTQTh                     |
| One-shot measurement     | FT, RTQTh                     | RTQTh                         |

Table I. The table classifies various approaches based on their regime of applications. Here STh, FT, and RTQTh represent the standard thermodynamics, the fluctuation theorem, and the resource theory of quantum thermodynamics respectively. The \(N\) denotes the number of particles in a system interacting with a thermal bath.

The resource theoretic formulation reveals that thermodynamics in the one-shot finite-size regime is not reversible and one needs many second laws, associated with many free energies, to characterize the transformations among the states that are block-diagonal in energy eigenbases \([8–10]\). These second laws have been further studied for more general states having superpositions in energy eigenstates \([11–13, 16]\). Recently, the approaches based on fluctuation theory and resource theory have been inter-connected in some cases \([17–19]\). However, all these investigations are limited to the situations, where the quantum system is interacting with only one thermal bath at a fixed temperature.

Can the second laws be formulated in case of heat engines operating in the one-shot finite-size regime, where a system composed of few quantum particles is interacting with two or more thermal baths at different temperatures? Apart from some efforts to quantify extractable work and engine efficiency in few special cases \([20–26]\), there has been no major progress, so far, in formulating second law for quantum heat engines in the one-shot finite-size regime.

With the precise characterizations of thermodynamical operations by introducing a first law for engines, we develop a resource theory for quantum and nano-scale heat engines, and formulate the second laws for quantum state transformation in presence two or multiple baths at different temperatures. We start by defining general thermodynamical operations in the quantum heat engines, which are more powerful than the ones considered earlier. These engine operations not only enable us to build a one-step Carnot heat engine but also enhances the work extraction efficiency in the one-shot finite-size regime. As revealed by this resource theoretic framework, the state transformations in a quantum engine are fundamentally irreversible and require many second laws to characterize. We also derive various statements of second laws, such as one-shot Clausius, Kelvin-Planck, and Carnot statements in the finite-size regime.

It is worth mentioning that much of the earlier works focus on how the a-thermal (non-equilibrium) property of a system can be converted into thermodynamical work, and, for that, one thermal bath is enough. On the contrary, here we develop a resource theory of quantum heat engines to address how, and to what extent, the heat can be converted into work in the one-shot finite-size regime. The formalism provides the foundation for a better theoretical understanding of the one-shot conversion of heat into work and the role of inter-system correlations in such processes. At the same time, it opens up new avenues to explore experimentally realizable quantum heat engines that have higher efficiency in the one-shot finite-size regime.

II. OPERATIONS IN QUANTUM HEAT ENGINES

A typical Carnot heat engine is comprised of two heat baths at different temperatures and a working system. The operations in such an engine involve four distinct steps in each cycle (see Figure 1), where the working system undergoes two isothermal transformations in contact with two different baths.

Figure 1. A schematic of the operations in a traditional Carnot heat engine. The engine is made up of one working system and two heat baths with inverse temperatures \(\beta_1 = 1/T_1\) and \(\beta_2 = 1/T_2\). We assume \(\beta_1 < \beta_2\). The engine operates in a cycle composed of four thermodynamically reversible steps: (a) First, an isothermal transformation \((\rho, H_{S_1}) \to (\sigma, H_{S_2})\) in interaction with the bath \(B_1\) at inverse temperature \(\beta_1\), where the state changes \((\rho \to \sigma)\) without updating the system Hamiltonian \(H_{S_1}\). (b) Second, an adiabatic transformation \((\sigma, H_{S_2}) \to (\sigma, H_{S_3})\) without any contact with the baths, where state remain unchanged but the system Hamiltonian modifies to \(H_{S_2} \to H_{S_3}\). (c) Third, an isothermal transformation \((\sigma, H_{S_3}) \to (\rho, H_{S_4})\) in interaction with the bath \(B_2\) at inverse temperature \(\beta_2\), only changing the state. (d) Finally, an adiabatic transformation \((\rho, H_{S_4}) \to (\rho, H_{S_1})\) without any interaction with the baths, and updating only the system Hamiltonian \(H_{S_4} \to H_{S_1}\).
and two adiabatic transformations in isolation. Instead, in a quantum heat engine, a system can interact with two baths semi-locally as shown in Figure 2. This leads to the more general semi-local thermal operations, as defined below. Interestingly, the four steps in a Carnot heat engine can be reduced to one step (see Figure 3) using these powerful operations.

**Definition 1** (Semi-local thermal operations (SLTOs)). Suppose a working system \( S_{12} \), composed of two subsystems \( S_1 \) and \( S_2 \), is (semi-locally) interacting with the baths \( B_1 \) and \( B_2 \) at inverse temperatures \( \beta_1 \) and \( \beta_2 \) respectively, as shown in Figure 2. Then, the thermodynamical operations on an arbitrary system state \( \rho_{S_{12}} \) in a quantum heat engine are defined as

\[
\Lambda_{S_{12}}(\rho_{S_{12}}) = \text{Tr}_{B_1B_2} \left[ U(\gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}})U^\dagger \right],
\]

with the condition that the global unitary \( U \) satisfies the commutation relation

\[
[U, \beta_1 H_{S_1B_1} \otimes I_{S_2B_2} + I_{S_1B_1} \otimes \beta_2 H_{S_2B_1}] = 0,
\]

where \( H_{B_xS_x} = H_{B_xB_x} \otimes I_{S_x} + I_{B_xB_x} \otimes H_{S_x} \), and \( H_{B_x} \) is the Hamiltonian of the bath \( B_x \), for \( x = 1, 2 \). The thermal states of baths are denoted by \( \gamma_{B_x} = \frac{e^{\beta_x H_{B_x}}}{\text{Tr}[e^{\beta_x H_{B_x}}]} \).

The resultant operations on the system \( S_{12} \) are semi-local in the sense that, even though the subsystems \( (S'_1 \) and \( S'_2) \) “selectively” interact with the baths \( (B_1 \) and \( B_2) \), the unitary \( U \) still allows certain interactions among them with the constraint (2).

For instance, it allows an energy exchange between the sub-system and bath composites so that

\[
\beta_1 \Delta E_1 + \beta_2 \Delta E_2 = 0,
\]

i.e., strict weighted-energy conservation, where \( \Delta E_1 \) and \( \Delta E_2 \) are the changes in the energies in the composites \( S_1B_1 \) and \( S_2B_2 \) respectively. The inverse temperatures \( \beta_1 \) and \( \beta_2 \) determine the rate at which the energy will transfer among the composites. Thus the condition (2) is the generalization of the first law for quantum heat engines, and it guarantees strict weighted-energy conservation. As it will be clear later, the first law ensures that no work can be created in spontaneous engine operation if the sub-systems \( S_1 \) and \( S_2 \) are initially in thermal equilibrium with the baths \( B_1 \) and \( B_2 \) respectively. Note, the SLTOs converge to the (local) thermal operations that are introduced in the resource theory of quantum states beyond thermal equilibrium presented in [6, 8, 10], when both the baths are of the same temperature, \( \beta_1 = \beta_2 \).

**Characterization of the semi-local thermal operations:** When the subsystems are locally in thermal equilibrium with the baths they are semi-locally interacting with, the corresponding joint uncorrelated state of the system \( S_{12} \) becomes \( \gamma_{S_1} \otimes \gamma_{S_2} \), where \( \gamma_{S_x} = e^{-\beta_x H_{S_x}}/Z_{S_x} \) with the partition functions \( Z_x = \text{Tr}[e^{-\beta_x H_{S_x}}] \). We term these states as the semi-Gibbs states, as both the local states are Gibbs states with different temperatures corresponding to the baths. The subsystems may assume arbitrary Hamiltonians and the set of all the corresponding semi-Gibbs states is denoted by the set \( \mathcal{T}_{S_{12}} \equiv \gamma_{S_1} \otimes \gamma_{S_2} \).

Then, for an arbitrary initial semi-Gibbs state \( \gamma_{S_{12}} \in \mathcal{T}_{S_{12}} \), (a) the semi-local thermal operations satisfy \( \Lambda_{S_{12}}(\gamma_{S_{12}}) \in \mathcal{T}_{S_{12}} \). Therefore, the SLTOs can transform semi-Gibbs states into semi-Gibbs states only, and this is the consequence of the restriction on the weighted-energy conservation in Eq. (3). (b) If any operation satisfies \( \Lambda_{S_{12}}(\gamma_{S_{12}}) \in \mathcal{T}_{S_{12}} \), then it can be implemented using the SLTOs (see Appendix D). (c) The SLTOs can implement the changes in the system Hamiltonians, say \( H_{S_{12}} \rightarrow H'_{S_{12}} = H'_S \otimes I + I \otimes H'_{S_2} \), with the help of clocks (see Appendix F3). These operations are nothing but the (semi-local) adiabatic transformations in a typical heat engine. In this framework, we are allowed to access a catalyst \( C_{12} \). The catalysts help to perform a broader class of semi-local thermal operations on a system, which is otherwise impossible. Note the catalyst remains unchanged before and after the process. Such operations are called catalytic semi-local thermal operations (cSLTOs) and are expressed as

\[
\Lambda_{S_{12};C_{12}}(\rho_{S_{12}} \otimes \rho_{C_{12}}) \rightarrow \sigma_{S_{12}} \otimes \rho_{C_{12}},
\]

where \( \rho_{C_{12}} \) is catalyst’s state (see Appendix C1). As mentioned, these catalytic operations form a larger set of operations compared to SLTOs that are also thermodynamically allowed operations in an engine. (d) It is interesting to note that the SLTOs are time-translation symmetric operations (see Appendix D2) with respect to the time evolutions generated by the subsystem Hamiltonians \( H_{S_1} \) and \( H_{S_2} \), as well as the weighted Hamiltonian given by

\[
H_{S_{12}}^{\beta_1 \beta_2} = \beta_1 H_{S_1} \otimes I + I \otimes \beta_2 H_{S_2}.
\]

That is why the SLTOs monotonically decreases the superpositions between different eigenstates of \( H_{S_{12}}^{\beta_1 \beta_2} \) or, in other words, among the weighted-energy eigenstates of the system \( S_{12} \). The cSLTOs also share the same property.

**III. MANY SECOND LAWS**

We introduce the general form of free-entropies, termed as \( \alpha \)-free-entropies, as the quantifiers of thermodynamic potential in a heat engine where the working system is composed.
of an arbitrary number of quantum particles. This enables us to study state transformation in a quantum heat engine in the one-shot finite-size regime.

Definition 2 \((\alpha\text{-free-entropies})\). Consider a system \(S_{12}\) in a state \(\rho_{S_{12}}\) block-diagonal in the eigenbasis of the weighted Hamiltonian \(H_{S_{12}}^{\alpha}\), and it is interacting with the baths as in Figure 2. Then the \(\alpha\)-free-entropy of \(\rho_{S_{12}}\) is expressed, for all \(\alpha \in [-\infty, \infty]\), as

\[
S_\alpha(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) = D_\alpha(\rho_{S_{12}} \parallel \gamma_S \otimes \gamma_S) - \log Z_1Z_2, 
\]

where the Rényi \(\alpha\)-relative entropy is given by \(D_\alpha(\rho \parallel \gamma) = \frac{\log \text{Tr}[\rho^\alpha \gamma^{1-\alpha}]}{\alpha-1}\). Here the thermal states of the subsystems are \(\gamma_S = e^{-\beta_S H_{S}}\), and the partition functions are \(Z_x = \text{Tr}[e^{-\beta_x H_{S1}}]\) for \(x = 1, 2\).

Note, we recover Helmholtz free-entropy \(S_1(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) = \beta_1 E_1 + \beta_2 E_2 - S(\rho_{S_{12}})\) for \(\alpha \to 1\), where \(E_{1/2} = \text{Tr} H_{S_{1/2}}\rho_{S_{12}}\) and \(S(\rho_{S_{12}})\) is the von Neumann entropy. Thus the \(\alpha\)-free-entropies are the one-shot generalizations of the Helmholtz free-entropies defined in the context of thermodynamics with multiple conserved charges, where the charges are mutually commutating and fully independent from each other, i.e., the states live in disjoint Hilbert spaces. With these \(\alpha\)-free-entropies, the transformations in a quantum heat engine can be characterized in terms of the second laws.

Second laws for states that are block-diagonal in weighted-energy: As we have mentioned, the cSLTOs are time-translation symmetric and monotonically decreases the superpositions between different weighted-energy eigenbases. Given that a heat engine operates in an arbitrarily large number of cycles, it is safe to assume that an arbitrary state will dephase to its block-diagonal form after some cycles. Therefore, we mainly focus on the transformations among states that are block-diagonal in the weighted-energy eigenbases. Although, we shall briefly discuss the situation when the states are not block-diagonal.

Consider a general transformation, via cSLTO,

\[
(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma'_{S_{12}}, H'_{S_{12}}),
\]

where along with the transformation among the states \(\rho_{12} \rightarrow \sigma'_{12}\) that are block-diagonal in the eigenbases of the weighted Hamiltonian \(H_{S_{12}}^{\alpha}\) given in Eq. (5), the initial non-interacting Hamiltonian \(H_{S_{12}} = H_{S_{12}}^{\alpha} \otimes \mathbb{I} + \mathbb{I} \otimes H_{S_{2}}\) of the system \(S_{12}\) is updated to \(H'_{S_{12}} = H'_{S_{12}}^{\alpha} \otimes \mathbb{I} + \mathbb{I} \otimes H'_{S_{2}}^{\alpha}\). Then the second laws that dictate such transformations are given in the theorem below (for proof, see Appendix F).

Theorem 3 (Second laws for block-diagonal states). Under cSLTO, the transformation in Eq. (7) is possible if, and only if,

\[
S_\alpha(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) \geq S_\alpha(\sigma'_{S_{12}}, \gamma_S' \otimes \gamma_S'), \quad \forall \alpha \geq 0,
\]

where \(\gamma_s = e^{-\beta^*_S H_{S}}\) and \(\gamma'_s = e^{-\beta'_S H_{S}}\), for \(x = 1, 2\).

For the transformation among the states that are not block-diagonal in the eigenbases of \(H_{S_{12}}^{\alpha}\), the above becomes only the necessary conditions where the corresponding dephased block-diagonal states have to satisfy (8). This necessary condition can be further supplemented with the monotonic decrease of quantum asymmetry (see Appendix G) present in the states, as cSLTOs are time translation symmetric operations.

Free-entropy distance, one-shot work, and fundamental irreversibility: Apart from dictating state transformations, the Theorem 3 delimits the amount of thermodynamic potential, i.e., free-entropy and work, can be extracted using a state transformation in an engine. It also quantifies the amount of the free-entropy required to be expended to make a transformation possible. Now the free-entropy distance is introduced to quantify these extractable free-entropy or free-entropy cost, in terms of the works that can be stored in a battery.

For that, a battery \(S_{W_{12}}\), with two sub-systems \(S_{W_1}\) and \(S_{W_2}\) and the non-interacting Hamiltonian \(H_{W_1} = H_{W_1} \otimes \mathbb{I} + \mathbb{I} \otimes H_{W_2}\) is introduced to store free-entropy (or work) once extracted. Without loss of generality, the battery subsystems are considered to be two-level systems with the Hamiltonians \(H_{W_1} = W_1 |W_1\rangle\langle W_1|_{S_{W_1}}\) and \(H_{W_2} = W_2 |W_2\rangle\langle W_2|_{S_{W_2}}\), and these are restricted to remain in pure state always. The \(S_{W_i}\) is tagged with subsystem \(S_1\) and similarly the \(S_{W_i}\) is with \(S_2\).

The initial battery state is chosen to be the zero-energy state \(|00\rangle_{S_{W_{12}}}, 0 \leq W_1 \leq \min(S, 0)\) is introduced to store free-entropy (or work) once extracted. Without loss of generality, the battery subsystems are considered to be two-level systems with the Hamiltonians \(H_{W_1} = W_1 |W_1\rangle\langle W_1|_{S_{W_1}}\) and \(H_{W_2} = W_2 |W_2\rangle\langle W_2|_{S_{W_2}}\), and these are restricted to remain in pure state always. The \(S_{W_i}\) is tagged with subsystem \(S_1\) and similarly the \(S_{W_i}\) is with \(S_2\).

Theorem 4 (Free-entropy distance). For the transformation in Eq. (7) via a cSLTO, the free-entropy distance between the initial and final states of the system is given by

\[
S_d(\rho_{12} \rightarrow \sigma'_{12}) = \beta_1 W_1 + \beta_2 W_2,
\]

where

\[
S_d(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) \geq \inf_{a \geq 0} \left[ S_a(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) - S_a(\sigma'_{S_{12}}, \gamma'_S \otimes \gamma'_S) \right].
\]

From this free-entropy distance, the one-shot work can be derived. Consider the transformation given in Eq. (7) via a cSLTO. If the initial state possesses larger free-entropy than the final one, i.e., \(S_a(\rho_{S_{12}}, \gamma_S \otimes \gamma_S) > S_a(\sigma'_{S_{12}}, \gamma'_S \otimes \gamma'_S)\) for all \(a \geq 0\), the transformation can take place spontaneously under cSLTOs. For this forward process, the \(S_d(\rho_{12} \rightarrow \sigma'_{12}) = \beta_1 W_1 + \beta_2 W_2 \geq 0\). Then, the guaranteed one-shot extractable work from the process is

\[
W_{ext} = W_1^f + W_2^f.
\]

In the special case where the final state is the semi-Gibbs state \(\sigma'_{S_2} = \gamma_{S_2}', \otimes \gamma_{S_2}', and the subsystem Hamiltonians do not change \(H'_{S_{12}} = H''_{S_{12}}\), the \(W_{ext}\) quantifies the one-shot distillable work from the state \(\rho_{S_{12}}\).
To perform the reverse transformation \((\rho_{S_{12}}, H'_{S_{12}}) \rightarrow (\rho_{S_{12}}, H_{S_{12}}))\), the Theorem 4 constrains that the minimum one-shot free-entropy to be supplied to ascertain the transformation is \(S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}}) \leq S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}})\), where equality holds for a few special cases. As a corollary, the extractable work from the transformation and the work cost to implement it are not equal and follow the inequality \(W_{ext} \leq W_{cost}\), where, again, the equality holds only in few cases. Therefore, there is fundamental irreversibility in quantum and nano-scale heat engines, in the one-shot finite-size regime. However, in the asymptotic limit, i.e., when the working system is composed of an asymptotically large number of particles, the reversibility is recovered as the equality in Eq. 12 and also \(W_{ext} = W_{cost}\) are achieved on average (see Appendix J).

It is worth mentioning that one-shot free-entropy cannot be extracted from the superpositions present in a state when it is expressed in the weighted-energy eigenbases. In other words, for a state \(\rho_{S_{12}}\) that satisfies \([\rho_{S_{12}}, H_{S_{12}}^{\rho,\beta_{1}}] \neq 0\), the thermodynamic potential stored in the superposition in the eigenbases of \(H_{S_{12}}^{\rho,\beta_{1}}\) cannot be accessed with the time-translation symmetric cSLTOs, in the one-shot finite-size regime. The only accessible free-entropy is the one corresponding to the dephased state of the original one (see Appendix G). Therefore, there is a free-entropy locking in the presence of such superposition. Note, in presence of quantum correlation, e.g., entanglement, such superposition is inevitably present in the state, and there would be free-entropy locking. However, in the asymptotic regime, where the number of particles in the system becomes considerably large, this free-energy can be unlocked and fully accessed via cSLTOs (see Appendix J for more details). As a result, one can fully extract free-entropy from the quantum correlations present in the system in the asymptotic regime.

\[ S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}}) \leq S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}}) \leq \beta_1 W_1^b + \beta_2 W_2^b. \]  

For \(\rho_{S_{12}} = \gamma_{S_{12}} \otimes \gamma_{S_{2}}\), and \(H_{S_{12}} = H'_{S_{12}}\), the \(W_{cost}\) represents the one-shot work cost of formation of the state \(\rho_{S_{12}}\).

Note, the thermodynamic reversibility is no longer respected when the working system is made up of a finite number of particles. This irreversibility can be understood from the fact that the free-entropy distance of a forward process is not in general equal to its reverse process, and

\[ S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}}) \leq -S_d(\rho_{S_{12}} \rightarrow \rho_{S_{12}}), \]

where equality holds for a few special cases. As a corollary, the extractable work from the transformation and the work cost to implement it are not equal and follow the inequality \(W_{ext} \leq W_{cost}\), where, again, the equality holds only in few cases. Therefore, there is fundamental irreversibility in quantum and nano-scale heat engines, in the one-shot finite-size regime. However, in the asymptotic limit, i.e., when the working system is composed of an asymptotically large number of particles, the reversibility is recovered as the equality in Eq. 12 and also \(W_{ext} = W_{cost}\) are achieved on average (see Appendix J).

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IV. QUANTUM AND NANO-SCALE HEAT ENGINES

The resource theoretic formalism presented above, in particular, the (catalytic) semi-local thermal operations, can be utilized to implement the operations in a Carnot engine in one-step, as shown in Figure 3. The one-step engine cycle involves the transformation \((\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\rho_{S_{12}}, H'_{S_{12}})\), via a cSLTO. Here the system Hamiltonian is modified to \(H_{S_{12}} = H_{S_{12}} \otimes \gamma_{S_{2}} \otimes \gamma_{S_{2}} \rightarrow H'_{S_{12}} = H'_{S_{12}} \otimes \gamma_{S_{2}} \otimes \gamma_{S_{2}}\), and satisfies the conditions \(\sigma'_{S_{12}} = U_{SWAP}^{S_{1} \rightarrow S_{2}}(\rho_{S_{12}})\), \(H'_{S_{1}} = H_{S_{1}}\), and \(H'_{S_{2}} = H_{S_{2}}\), where the unitary \(U_{SWAP}^{S_{1} \rightarrow S_{2}}\) performs a SWAP operation between sub-systems \(S_{1}\) and \(S_{2}\). Clearly, this one-step engine cycle is more general and powerful than the ones considered earlier. Moreover, it allows the presence of correlations between the subsystems \((S_{1}\) and \(S_{2}\)) of the working system \(S_{12}\). The repeatability conditions in engine operation impose restrictions on the transformations in the states of the working system and the Hamiltonians of the subsystems, unlike the more general ones considered in Eq. (7). Thus, the second laws, given in Theorem 3, and the fundamental irreversibility remain applicable.

Statements of second laws for heat engines: In classical thermodynamics, we often encounter various statements of second law in terms of heat, e.g., Clausius, Kelvin-Plank, and Carnot statements of the second law. We can generalize these
statements in the one-shot finite-size regime using the present framework but in terms of work.

For the one-step spontaneous engine cycle with the transformation in Eq. (13), the free-entropy distances between the states before and end of the cycle, by Theorem 4, is

$$\beta_1 W_1 + \beta_2 W_2 \geq 0,$$  \hspace{1cm} (14)

where the $W_1$ and $W_2$ are the one-shot works. The $W_1$ and $W_2$ are the works involved while the system $S_{12}$ is semi-loca-ly interacting with the baths $B_1$ and $B_2$ respectively. Since $\beta_1 < \beta_2$, it must satisfy $W_1 \geq 0$ and $W_2 \leq 0$. The Eq. (14) encodes all statements of second law in the one-shot finite-size regime, as given in the corollary below.

**Corollary 5 (One-shot statements of second law).** An engine, working in a cycle using the step given in Eq. (13) and operates spontaneously. Then, for $\beta_1 < \beta_2$, the one-shot statements are given as follows.

Clausius statement: The one-shot work extracted $(W_1)$ in contact with hot bath at $\beta_1$ is larger than the one-shot work $(W_2)$ expended in interaction with the cold bath at $\beta_2$, i.e., $W_1 + W_2 > 0$.

Kelvin-Planck statement: The net extractable one-shot work is strictly less than the one-shot work extracted in presence of hot bath at $\beta_1$, i.e., $W_{\text{ext}} = W_1 + W_2 < W_1$.

Carnot statement: The one-shot efficiencies of work extraction in every engine cycle are given by

$$\eta_1 = \frac{W_{\text{ext}}}{W_1} \geq 1 - \frac{\beta_1}{\beta_2}, \quad \eta_2 = \frac{W_{\text{ext}}}{W_2} \leq \frac{\beta_2}{\beta_1} - 1.$$  \hspace{1cm} (15)

Traditionally the statements are expressed in terms of heat. For a system with an asymptotically large number of particles, the heat is well defined. However, in the one-shot finite-size regime, it is not the case. Rather, the work can only be defined precisely. That is why, we use one-shot work to express the statements, and the Carnot efficiency appears somewhat different than the traditional one. Nevertheless, it conceptually captures and generalizes the essence of the second law in the one-shot finite-size regime. Since the thermodynamics is not reversible in this regime, the extracted work is less and the work cost is more compared to an engine working in the asymptotic regime. Hence, in general, the engine efficiency in one-shot finite-size regime is lower than the efficiency in the asymptotic regime.

One may recover the statements in terms of heat, where the heat $Q$ is defined as $Q = \Delta E - W$. Here $\Delta E$ is the change in the internal energy in the system and $W$ is the work done by the system. Then, by using the Eqs. (3) and (14), we have

$$\beta_1 Q_1 + \beta_2 Q_2 \leq 0,$$  \hspace{1cm} (16)

where $Q_{1/2} = \Delta E_{1/2} - W_{1/2}$. The expression above is the Clausius inequality and mathematically captures all the statements in terms of heat. In the asymptotic regime, where the above definition of heat is applicable, we recover the traditional form of Carnot efficiency as $\eta = \frac{W_{\text{ext}}}{Q_1} \leq \frac{Q_1 + Q_2}{Q_1} \leq 1 - \frac{\beta_1}{\beta_2}$, where the extracted work is given by $W_{\text{ext}} \leq Q_1 + Q_2$ and equalities only hold for the reversible engine operations.

Like for many second laws based on $\alpha$-free-entropies in Theorem 3, we can also derive many $\alpha$ dependent statements of many second laws. Consider that the initial working system is initially uncorrelated $\rho_{S_{12}} = \rho \otimes \sigma$ in an engine. Then the one-step engine transformation, given in Eq. (13), reduces to

$$\rho \otimes \sigma, \quad H_{S_{12}} \rightarrow (\sigma \otimes \rho, \, H'_{S_{12}}),$$  \hspace{1cm} (17)

where $H'_{S_{12}} = H_{S_1} \otimes I + I \otimes H_{S_2}$ and $H'_{S_{12}} = H_{S_1} \otimes I + I \otimes H_{S_2}$. In this transformation, there are two sub-transformations happening simultaneously via a cSLTO: (i) forward sub-transformation, $(\rho, H_{S_1}) \rightarrow (\sigma, H'_{S_1})$ in presence of the bath $B_1$ at inverse temperature $\beta_1$, and (ii) the reverse sub-transformation $(\sigma, H_{S_2}) \rightarrow (\rho, H'_{S_2})$ while interacting with bath $B_2$ at inverse temperature $\beta_2$.

For the uncorrelated state $\rho_{S_{12}} = \rho \otimes \sigma$, the $\alpha$-free-entropy becomes additive $S_a(\rho \otimes \sigma, \gamma_{S_1} \otimes \gamma_{S_2}) = S_a(\rho, \gamma_{S_1}) + S_a(\sigma, \gamma_{S_2})$, where $S_a(\rho, \gamma_{S_1}) = D_a(\rho, \| \gamma_{S_1}) - \log Z_{\rho}$ The $S_a(\rho, \gamma_{S_1})/\beta_1$ are the accessible $\alpha$-free energy stored in the system $\rho_{S_1}$, which can be converted into work using a (local) thermal operation in presence of a bath at inverse temperature $\beta_2$ [10]. The second laws, considering the sub-transformations (i) and (ii) simultaneously occur via a cSLTO, imply

$$\beta_1 W_1^{(\alpha)} + \beta_2 W_2^{(\alpha)} \geq 0, \quad \forall \alpha > 0,$$  \hspace{1cm} (18)

where the $W_i^{(\alpha)}$ quantifies the change in $\alpha$-work due to the transformation in the presence of the bath at inverse temperature $\beta_2$. In terms of the $\alpha$-free energies [10], we express these $\alpha$-works as

$$W_1^{(\alpha)} = \frac{1}{\beta_1} S_a(\rho, \gamma_{S_1}) - S_a(\sigma, \gamma'_{S_1}),$$  \hspace{1cm} (19)

$$W_2^{(\alpha)} = \frac{1}{\beta_2} S_a(\sigma, \gamma_{S_2}) - S_a(\rho, \gamma'_{S_2}),$$  \hspace{1cm} (20)

where $\gamma_{S_1} = e^{\gamma_{S_1}}$, $\frac{1}{\beta_1} [e^{\gamma_{S_1}}]$, and $\gamma'_{S_1} = e^{\gamma'_{S_1}}$, $\frac{1}{\beta_1} [e^{\gamma'_{S_1}}]$. Given $\beta_1 < \beta_2$ and a spontaneous engine cycle, the Eq. (18) guarantees that $W_1^{(\alpha)} = W_1^{(\alpha)} + W_2^{(\alpha)} > 0$, $\forall \alpha > 0$. Recall, unlike the one-shot works, the one-shot heats are not well defined. So, with the help of $\alpha$-works, we generalize various statements of the second law in the one-shot finite-size regime.

**Corollary 6 (Many statements of many second laws).** An engine, working in a cycle using the step given in Eq. (17) and operates spontaneously. Then, for all $\alpha > 0$ and $\beta_1 < \beta_2$, the $\alpha$-statements are given below.

Clausius $\alpha$-statements: $W_1^{(\alpha)} + W_2^{(\alpha)} > 0$.

Kelvin-Planck $\alpha$-statements: $W_{\text{ext}} = W_1^{(\alpha)} + W_2^{(\alpha)} < W_1^{(\alpha)}$.

Carnot $\alpha$-statements: The $\alpha$-efficiencies are given by

$$\eta_1^{(\alpha)} = \frac{W_{\text{ext}}^{(\alpha)}}{W_1^{(\alpha)}} \geq 1 - \frac{\beta_1}{\beta_2}, \quad \eta_2^{(\alpha)} = \frac{W_{\text{ext}}^{(\alpha)}}{W_2^{(\alpha)}} \leq \frac{\beta_2}{\beta_1} - 1.$$  \hspace{1cm} (21)
Note, the guaranteed one-shot free-entropy gain in the one-step cycle given in Eq. (17), using cSLTOs, is
\[
\beta_1 W_1 + \beta_2 W_2 = \inf_{\alpha_1, \alpha_2 \in \mathbb{R}} \left[ \beta_1 W^{(\alpha_1)}_1 + \beta_2 W^{(\alpha_2)}_2 \right] \geq 0. \tag{22}
\]

Let us now show that the one-shot efficiency of the Carnot engine operating via cSLTOs is larger, in general, compared to the case considered in Figure 1, where the system locally interacts with individual baths at a time. Suppose that the system locally interacts with the baths using local thermal operations \([6, 8, 10]\) and undergoes two sub-transformations (i) and (ii) in separate steps to complete the Carnot cycle, as discussed earlier. For these sub-transformations (i) and (ii), the one-shot extractable work and the work cost under local thermal operations, respectively, are
\[
\tilde{W}_1 = \inf_{\alpha_1 \in \mathbb{R}} [W^{(\alpha_1)}_1] \leq W_1, \quad \text{and} \quad \tilde{W}_2 = \sup_{\alpha_2 \in \mathbb{R}} [W^{(\alpha_2)}_2] \geq W_2. \tag{23}
\]

With the one-shot extracted work \(W_{\text{ext}} = \tilde{W}_1 + \tilde{W}_2\), the Carnot efficiencies of the engine are then
\[
\tilde{\eta}_1 = \frac{W_{\text{ext}}}{\tilde{W}_1} \leq \eta_1, \quad \tilde{\eta}_2 = \frac{W_{\text{ext}}}{\tilde{W}_2} \leq \eta_2, \tag{24}
\]
which are less than the efficiencies for engines operating with one-step cycle using catalytic semi-local thermal operations or cSLTOs.

V. CONCLUSIONS

The laws of thermodynamics were initially developed on the basis of empirical observations of the transformation happens in heat engines that convert heat into work. Then thermodynamics for a large number of particles has been founded on the basis of statistical mechanics. With the emergence of quantum mechanics, understanding of quantum and nano-scale systems, and the development of information theories, tremendous efforts have been made to explore thermodynamics in the quantum domain, as well as in the finite number of particles regime. There are two major lines of approaches. One is based on fluctuation theorem steaming from statistical mechanics and open quantum system dynamics \([1–3, 18]\), and the other approach is based on the resource theory \([6, 8, 10]\) – a framework developed to characterize quantum entanglement in information theory.

Here we consider the information-theoretic approach to formulate the laws that govern the transformation occur in the quantum and nano-scale heat engines, and that leads us to formulate resource theory of quantum heat engines. The previously introduced resource theory of quantum systems away from thermal equilibrium \([6, 8, 10]\) deals with the conversion of thermodynamic potentials (a-thermality) into work, in the presence of a single bath. While, in this work, we have formulated a resource theory that addresses the conversion of heat into work in the one-shot finite-size regime. A quantum engine is composed of a (bipartite) system, as the working system, and two large baths at different temperatures. The subsystems semi-locally interact with the baths. Furthermore, the energy exchange between the hot bath to the cold bath has to respect an additional constraint, that is the global operation on the system and baths has to satisfy strict weighted-energy conservation. This restriction in energy flow constitutes the first law for quantum heat engines, and the semi-local thermal operations or the engine operations, are exactly the reduced quantum operations applied on the system. These generalized and powerful engine operations have allowed us to construct a Carnot heat engine that operates in a one-step cycle. Furthermore, as we have shown, the SLTOs also allows us to achieve higher one-shot engine efficiency.

With this precise definition of engine operations, we have established many second laws of quantum heat engines. These second laws are more general and are applicable to the engines with a working system composed of a finite number of particles, i.e., one-shot finite-size regime, where the formalism based on statistical mechanics becomes untenable. This enables us to quantify one-shot extractable work in an engine and one-shot work cost to run a refrigerator. We show that, unlike in the asymptotic regime, quantum thermodynamics in the one-shot finite-size regime is not reversible. Therefore, there is a fundamental irreversibility in the quantum regime. Various forms of the second law, in terms of Clausius, Kelvin-Planck and Carnot statements, are also generalized to the one-shot finite-size regime using one-shot work in an engine. This leads to many one-shot statements of many second laws. Note, the formalism and the laws can be easily extended to the engines operating with arbitrarily many baths at different temperatures.

Due to the time-translation symmetry of the allowed operations in engines, the derived second laws can fully characterize the transformations of the working systems that are block-diagonal in energy bases. Otherwise, the laws remain only the necessary conditions for the engine transformations. There is a work-locking in presence of quantum correlation, where there are non-block-diagonal elements in the density matrix expressed in the weighted-energy eigenstates, as one-shot work can only be extracted from the block-diagonal part of the original state. Note, the block-diagonal states can possess classical correlations. These states are sufficient to characterize an engine which repeats its cycle many times. Consequently, one may construct a heat engine that exclusively exploits the classical correlation to convert heat into work. For that, one needs an initial correlated bipartite system in the state \(\rho^{S_{12}} = \tau_{AB}\) and the final state \(\sigma^{S_{12}} = \tau_a \otimes \tau_B\), where \(\tau_{AB} = \text{Tr}_{B/A}[\tau_{AB}]\) before and after the one-step cycle respectively.

In the asymptotic regime, the work-locking in the quantum correlations is lifted. This is due to the asymptotic equipartition theorem, and the fact that arbitrary states become time-translation symmetric in the asymptotic regime. Therefore, in this regime, an engine can exclusively exploit quantum correlations, e.g., entanglement, to convert heat into work. It is known that strong quantum correlations can lead to anomalous heat flow from a colder bath to a warmer bath \([14]\). This is nothing but a refrigeration process driven by the free-entropy stored in the correlation. The present formalism can thus fully explain this anomalous heat flow and can exploit
this feature in developing correlation driven quantum engines.

Unlike other approaches, the resource theoretic formalism in presence of single bath [6, 10, 27] or in presence of multiple baths at different temperatures considered here, the thermodynamically allowed operations are the restricted ones. The restrictions are imposed due to the strict energy or weighted-energy conservations, i.e., the first law, and these ensure proper counting of energy flow. Though the approaches are clean in the theoretical sense, the local or semi-local thermal operations are difficult to implement. However, there have been various proposals exploring possible physical realizations of (local) thermal operations in the presence of a single bath, see for example [28–30]. Following a similar track, it can also be possible to implement semi-local thermal operations, i.e., the engine operations in the presence of multiple baths. This will certainly open up the possibility to experimentally realize quantum heat engines operating in a one-step cycle and with higher one-shot efficiencies in finite-size regime.

In summary, our work lays a basis for a deeper theoretical understanding and a possibility of experimentally realizable quantum heat engines. Thus, it will be instrumental to explore new avenues for future quantum technologies.

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APPENDIX

Below we provide all the information needed to supplement and elaborate the results outlined in the main text.

Appendix A: Thermal baths and system-bath composites

The goal of this section is to characterize the Hilbert spaces of considerably large bath(s) at certain temperature(s), small systems that are in and away from thermal equilibrium, and their composites.

1. Some useful properties of baths

There are several useful properties of a considerably large bath, compared to the systems it interacts with. A bath is considered to be always in thermal equilibrium at a fixed temperature, even after it interacts with a system. Therefore it has to be reasonably large so that it almost does not change after the interaction and remain in equilibrium. So, a bath being large is an important assumption.

All the systems, we consider, have Hamiltonians bounded from below, i.e., with the lowest energy is zero. The largest energy of the bath Hamiltonian $H_B$ is $E_{\text{max}}^B \rightarrow \infty$. The heat bath always remains in a Gibbs state $ho_B = e^{-\beta H_B} / \text{Tr}[e^{-\beta H_B}]$ with inverse temperature $\beta$. There exists a set of energies $\mathcal{E}$ in which the bath lives with high probability. Mathematically, for the projector $P_E$ that spans over the space with a set of energies $E$, this is expressed as

$$\text{Tr}[P_E \rho_B] \geq 1 - \delta,$$

where $\delta > 0$. Given this, the bath satisfies the following properties [8]:

- The energy $E \in \mathcal{E}$ is peaked around a mean value as $E \in (\langle E \rangle - O(\sqrt{E}), \ldots, \langle E \rangle + O(\sqrt{E}))$.
- The degeneracies $g_B(E)$ in the energies $E \in \mathcal{E}$ scale exponentially with $E$, i.e., $g_B(E) \geq e^{\beta E}$, where $\beta$ is a constant.
- Consider any three energies $E_b, E_s$ and $E_s'$ so that $E_b \in \mathcal{E}$, $E_s \ll E_b$, and $E_s' \ll E_b$. Then there exists an $E_b' \in \mathcal{E}$ such that $E_b + E_s = E_b' + E_s'$.
- For an energy $E_b \in \mathcal{E}$, the degeneracies satisfy $g_B(E_b + E_s) \approx g_B(E_b)e^{\beta E_s}$.

These properties are instrumental in understanding the thermodynamics of quantum and nano-scale systems interacting with large baths.

2. One system and one bath

Characterization of Hilbert space composed of a small system $S$ and a considerably large thermal bath $B$ at inverse temperature $\beta = 1/T$, and the structures of the joint states can be found in details in [8]. Here we shall re-iterate the properties briefly so that these help us to smoothly extend the formalism to the Hilbert spaces composed of two or more systems and thermal baths at different temperatures.

Assume a considerably large bath $B$ and a reasonably small system $S$ that are jointly in a state $\rho_B \otimes \rho_S$. The bath’s Hamiltonian $H_B$ is bounded from below and the largest energy could be very large, $E_{\text{max}}^B \rightarrow \infty$. The system Hamiltonian $H_S$ is also bounded
from below and \( E_{S,\max}^B \ll E_{S,\max}^B \). Here we assume non-degenerate \( H_S \). Extension to degenerate \( H_S \) can be followed easily. Now the underlying Hilbert space \( \mathcal{H}_B \otimes \mathcal{H}_S \) is written as the Kronecker sums of constant total-energy sub-spaces, i.e.,

\[
\mathcal{H}_B \otimes \mathcal{H}_S = \bigoplus_E \left( \bigotimes_{E_S} \mathcal{H}^{E-E_S}_B \otimes \mathcal{H}^{E_S}_S \right),
\]

where total energy \( E = E_B + E_S \). Therefore, an arbitrary joint bath-system state that is diagonal in energy eigenbases can be written as

\[
\rho_B \otimes \rho_S = \sum_E P_{EB} \otimes \rho_S P_E,
\]

where \( P_E \) are the constant energy projectors acting on the joint system-bath space. After the projection, the non-normalized joint state becomes \[8\]

\[
P_{EB} \otimes \rho_S P_E \approx \frac{g_B(E)e^{-\beta E}}{Z_B} \sum_{E_S} \frac{1}{g_B(E)e^{-\beta E_S}} \otimes P_{E_S} \rho_S P_{E_S}.
\]

Here \( Z_B \) is the partition function, and \( g_B(E) \) is the degeneracy of the bath energy \( E \) at inverse temperature \( \beta \). After normalization, the state is written as

\[
\rho_{ES}^E = \frac{1}{p_E} P_{EB} \otimes \rho_S P_E,
\]

\[
\approx \bigoplus_{E_S} \eta_{E-E_S} \otimes P_{E_S} \rho_S P_{E_S},
\]

where \( p_E = \text{Tr}(P_{EB} \otimes \rho_S) \) and \( \eta_{E-E_S} = \frac{1}{g_B(E)e^{-\beta E_S}} \).

When a system is attached with a bath, thermalization or a process of work extraction, in general, leads the system close to its corresponding thermal state. Once thermalized, the system state becomes \( \gamma_S = \frac{\rho_E}{Z_S} \), where \( Z_S \) is the partition function. Then the joint normalized system-bath state, of fixed total energy \( E \), reduces to

\[
\sigma_{ES}^E \approx \frac{1}{g_B(E)Z_S^E} \eta_{E-E_S}.
\]

Below, we extend this formalism to characterize the Hilbert space and states of the system-bath composite to the cases where there are more systems and more baths with different temperatures.

3. In presence of two baths with different temperatures

Without loss of generality we consider a bipartite system \( S_{12} \) with two subsystems, \( S_1 \) and \( S_2 \), that are semi-locally interacting with two baths \( B_1 \) and \( B_2 \) respectively where he baths are with the inverse temperatures \( \beta_1 \) and \( \beta_2 \). We skip the discussion on the notion of `semi-local’ here. We elaborate on it in the next section where we shall characterize the thermodynamics operations that are applicable in a quantum heat engine.

Say, the two considerably large baths \( B_1 \) and \( B_2 \) are with Hamiltonians \( H_{B_1} \) and \( H_{B_2} \) respectively. Further, the small systems \( S_1 \) and \( S_2 \) are the subsystems of a bipartite system \( S_{12} \) with the Hilbert space \( \mathcal{H}_{S_{12}} = \mathcal{H}_{S_1} \otimes \mathcal{H}_{S_2} \). The system \( S_{12} \) possesses a non-interacting Hamiltonian \( H_{S_{12}} = H_{S_1} \otimes I_{S_2} + I_{S_1} \otimes H_{S_2} \). The bath Hamiltonians \( H_{B_{1/2}} \) are bounded from below and could have \( E_{B_{1/2}}^\text{max} \to \infty \). The system Hamiltonians \( H_{S_{1/2}} \) are also bounded from below and satisfy \( E_{S_{1/2}}^\text{max} \ll E_{B_{1/2}}^\text{max} \). We consider here non-degenerate system Hamiltonians \( H_{S_{1/2}} \). Extension to degenerate cases can be done easily.
Similarly, set of energies $\nu_1$ where $\gamma$ where $\gamma_1$ where the projectors on the system ($S_1$) in which the bath $B_1$ lives with high probability and satisfy the properties mentioned for Eq. (A1). Consequently, any system-baths joint state can be written in terms of fixed total energy blocks. A system-baths state $\rho_{B_1 \otimes B_2 \otimes S_1 \otimes S_2}$, which is diagonal in the energy eigenbases, can be expressed as

$$\gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}} = \sum_{E_1 + E_2} P_{E_1 + E_2} \left( \gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}} \right) P_{E_1 + E_2} = \sum_{E_1 + E_2} P_{E_1 + E_2} P_{E_1 + E_2},$$

where $P_{E_1 + E_2}$s are the projectors with energy $E_1 + E_2$ and $P_{E_1 + E_2} = \text{Tr} \left[ P_{E_1 + E_2} (\gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}}) \right]$ are the probabilities. Note, $P_{E_1 + E_2} = P_{E_1} \otimes P_{E_2}$.

Say the set of energies $E_1$ in which the bath $B_1$ lives with high probability and satisfy the properties mentioned for Eq. (A1). Similarly, set of energies $E_2$ in which the bath $B_2$ lives with high probability. Then, for $E_1 \in E_1$ and $E_2 \in E_2$, the normalized joint state $\rho_{E_1 + E_2}$ after projection with $P_{E_1 + E_2}$ is

$$P_{E_1 + E_2} = \frac{1}{P_{E_1 + E_2}} P_{E_1 + E_2} \left( \gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}} \right) P_{E_1 + E_2} \approx \sum_{E_1 + E_2} \eta_{E_1 - E_1 + E_2 - E_2} \otimes P_{E_1 + E_2} \rho_{S_{12}} P_{E_1 + E_2},$$

where the projectors on the system ($S_{12}$) space are $P_{E_1 + E_2} = P_{E_1} \otimes P_{E_2}$, and

$$\eta_{E_1 - E_1 + E_2 - E_2} = \frac{\gamma_1}{\gamma_{E_1 - E_1}} \otimes \frac{\gamma_2}{\gamma_{E_2 - E_2}} = \frac{\gamma_1}{g_{B_1}(E_1)e^{-\beta_1 E_1}} \otimes \frac{\gamma_2}{g_{B_2}(E_2)e^{-\beta_2 E_2}}.$$

With these minimum tools in hand, we move on to introduce semi-local thermal operations that are applicable to the heat engines operating between two baths at different temperatures. But, before that, we shall introduce the thermodynamical operation, i.e., thermal operation, in the presence of one bath below.

**Appendix B: Thermal operations: presence of single bath**

Traditionally, in thermodynamics, the thermal operations are those that keep a thermalized system unchanged upon application. It is also expected that the thermal operations bring a non-equilibrium system closer to its thermalized state. However, there are many prescriptions to identify the set of thermal operations, for a given temperature. In the recent formulation of quantum thermodynamics – the resource theory of quantum thermodynamics [6, 8, 10] – the thermal operations are characterized based on microscopic notion first law of thermodynamics, that is the system-bath composite are allowed to interact through a certain unitary operations that ”strictly” conserve the total energy of the system and bath.

Suppose a small system $S$ interacting with considerably large bath $B$ at temperature $T = \frac{1}{\beta}$. The $H_S$ and $H_B$ are the system and bath Hamiltonians respectively. Then the thermal operations, applied on a system state $\rho_S$, can be expressed in terms of Stinespring dilation, as

$$A(\rho_S) := \text{Tr}_B \left[ U_{SB}(\rho_S \otimes \gamma_B) U_{SB}^\dagger \right],$$

where $\gamma_B$ is the thermal operation, in the presence of one bath below. The underlaying joint Hilbert space correspond to the $S_{12}$, $B_1$, and $B_2$ is now $\mathcal{H}_{B_1} \otimes \mathcal{H}_{B_2} \otimes \mathcal{H}_{S_1} \otimes \mathcal{H}_{S_2}$. Here we assume the systems to interact as in Figure 5. It can be expressed as the Kronecker sums of constant total-energy sub-spaces, i.e.,

$$\mathcal{H}_{B_1} \otimes \mathcal{H}_{B_2} \otimes \mathcal{H}_{S_1} \otimes \mathcal{H}_{S_2} = \bigoplus_{E_1 + E_2} \mathcal{H}_{E_1 - E_{12}}^{E_1} \otimes \mathcal{H}_{E_2 - E_{12}}^{E_2} \otimes \mathcal{H}_{S_1}^{E_{12}} \otimes \mathcal{H}_{S_2}^{E_{12}},$$

where $E_1 = E_{B_1} + E_{S_1}$ and $E_2 = E_{B_2} + E_{S_2}$. Temperatures of the baths are $T_1 = \frac{1}{\beta_1}$ and $T_2 = \frac{1}{\beta_2}$.
where the unitary satisfies the commutation relation $[U_{SB}, H_S \otimes 1_B + 1_S \otimes H_B] = 0$, the $\gamma_B = \frac{e^{\beta_B H_B}}{Tr[e^{\beta_B H_B}]}$ is the thermal state of the bath $B$.

**First law:** Here the $[U_{SB}, H_S \otimes 1_B + 1_S \otimes H_B] = 0$ is the first law in the quantum domain, which ensures the *strict* conservation of not only in the first moment but also any other arbitrary moment of total energy. This is important for a regime where the number of systems is finite in number and the uncertainty in energy is reasonably large compared to the mean energy of the system and cannot be ignored.

The thermal operations satisfy the desired *Gibbs* preserving property

$$\Lambda(\gamma_S) \in \mathcal{T}, \quad (B2)$$

where $\gamma_S$ is the thermal state of the system $S$, and $\mathcal{T} = \{\gamma_S\}$ is the set of all thermal states with arbitrary Hamiltonian at temperature $T$.

With the characterization of thermal operations, as the allowed operations, and thermal states as the resourceless states, an elegant resource theory has been developed [6, 8, 10] for quantum states away from thermal equilibrium. This powerful framework and its later extensions lead to a newer understanding of thermodynamics at the quantum level.

**Appendix C: Semi-local thermal operations: presence of two baths at different temperatures**

The situation becomes complicated in the presence of multiple baths at different temperatures. There exists no quantum system that is simultaneously in equilibrium with all the baths. Thus, finding a set of operations that keep certain states unchanged is tricky.

In characterizing such operations, we consider the situations that naturally occur in quantum heat engines. Typically a heat engine is composed of two considerably large heat baths at different temperatures. There is also a working system, that borrows and releases heat from the baths. A schematics of such engines are depicted in Fig. 5. A battery can also be attached, as part of the system, which could store or expend work. Say, the two thermal baths are $B_1$ and $B_2$ with inverse temperatures $\beta_1$ and $\beta_2$ (or the temperatures $T_1$ and $T_2$) respectively. The working system is $S_{12}$.

In this setup, we assume that the bipartite working system $S_{12}$ is composed of two sub-systems $S_1$ and $S_2$ with non-interacting Hamiltonian

$$H_{S_{12}} = H_{S_1} \otimes 1_{S_2} + 1_{S_1} \otimes H_{S_2}. \quad (C1)$$

The working system $S_{12}$ is in an arbitrary state $\rho_{S_{12}}$ and could have correlation among the sub-systems. The sub-system $S_1$ ($S_2$) semi-locally interacts with bath $B_1$ ($B_2$). When the sub-system $S_1$ thermalizes to the inverse temperature $\beta_1$, the resultant equilibrium state becomes

$$\gamma_{S_1} = e^{-\beta_1 H_{S_1}}/Tr\left(e^{-\beta_1 H_{S_1}}\right). \quad (C2)$$

Similarly, once thermalized to the inverse temperature $\beta_2$, the sub-system $S_2$ is transformed to

$$\gamma_{S_2} = e^{-\beta_2 H_{S_2}}/Tr\left(e^{-\beta_2 H_{S_2}}\right). \quad (C3)$$

The joint uncorrelated thermal state (with corresponding different local inverse temperatures) becomes $\gamma_{S_1} \otimes \gamma_{S_2}$. For a different non-interacting system ($S_{12}$) Hamiltonian, i.e., $H'_{S_{12}} = H'_{S_1} \otimes 1_{S_2} + 1_{S_1} \otimes H'_{S_2}$, the corresponding thermal states, of the sub-systems $S_1$ and $S_2$ become $\gamma'_{S_1} = e^{-\beta_1 H'_{S_1}}/Tr\left(e^{-\beta_1 H'_{S_1}}\right)$ and $\gamma'_{S_2} = e^{-\beta_2 H'_{S_2}}/Tr\left(e^{-\beta_2 H'_{S_2}}\right)$. Then, the joint uncorrelated thermal state (with corresponding local inverse temperatures) is $\gamma'_{S_1} \otimes \gamma'_{S_2}$. For all possible non-interacting system Hamiltonians (as in Eq. (C1)), the set of such joint uncorrelated thermal states is represented by $\mathcal{T}_{S_{12}}$, i.e.,

$$\gamma_{S_1} \otimes \gamma_{S_2} \in \mathcal{T}_{S_{12}}. \quad (C4)$$

Now onward we refer the states $\gamma_{S_1} \otimes \gamma_{S_2} \in \mathcal{T}_{S_{12}}$ as the *semi-Gibbs* states.

The semi-local thermal operations (SLTOs) can be implemented (in the form of Stinespring dilation) with access to the thermal baths and help of unitaries, as in the following.

**Definition 7** (Stinespring dilation of semi-local thermal operations). *An arbitrary semi-local thermal operation, applied on a system $S_{12}$ with the non-interacting Hamiltonian as in Eq. (C1) and in a joint state $\rho_{S_{12}}$, is given by*

$$\Lambda_{S_{12}}(\rho_{S_{12}}) = Tr_{B_1 B_2} [U_{BS} (\gamma_B \otimes \gamma_B \otimes \rho_{S_{12}}) U_{BS}^\dagger], \quad (C5)$$

where the global unitary $U_{BS}$ satisfies

$$[U_{BS}, \beta_1 H_{B_1 S_1} \otimes 1_{B_2 S_2} + 1_{B_1 S_1} \otimes \beta_2 H_{B_2 S_2}] = 0, \quad (C6)$$

where $H_{B_1 S_1} = H_{B_1} \otimes 1_{S_1} + 1_{B_1} \otimes H_{S_1}$ and $H_{B_2 S_2} = H_{B_2} \otimes 1_{S_2} + 1_{B_2} \otimes H_{S_2}$. 
An interesting fact to note that these operations are not necessarily locally thermal correspond to local inverse temperatures $\beta_1$ or $\beta_2$, thus the notion semi-local. For the thermal operations in the presence of a single heat bath, as mentioned in Section B, the unitaries are restricted to the ones that commute with joint non-interacting system and bath Hamiltonians. By this imposition, a strict total (system and bath) energy conservation, hence the first law, is ensured. The temperature does not enter directly in the commutation relation. Rather, the temperature dependence of thermal operation indirectly enters through the baths state.

**First law for quantum engines:** Contrary to the single bath case, in semi-local thermal operations in presence of two baths with different temperatures, the temperatures enter in two ways: (i) through the choice of thermal baths as in Eq. (C5) and (ii) the unitaries that are restricted by commutation relation in Eqs. (C6). This commutation relation (C6) is, in fact, the modified version of first law for a quantum heat engine, as one may argue, in the presence of multiple baths with different temperatures.

Consider the situation, where the unitary in Eq. (C5) satisfies

$$[U_{BS}, \beta_1 H_{B,S_1} \otimes I_{B,S_2}] = 0,$$

$$[U_{BS}, I_{B,S_1} \otimes \beta_2 H_{B,S_2}] = 0.$$  

(C7) \hspace{1cm} (C8)

Clearly, fulfillment of the above also ensures the commutation relation (C6). The commutation relations in (C7) and (C8) imply strict energy conservation of each composite $B_1S_1$ and $B_2S_2$ separately, and restrict any exchange of energy between $B_1S_1$ and $B_2S_2$ composites. Given this constraint, the resulting operations on the systems $S_1$ and $S_2$ become nothing but the local thermal operations as outlined in B.

Any unitary $U_{BS}$ that satisfies (C6) and does not satisfy (C7) and (C8), allows an energy exchange between the sub-system and bath composites. A change in the (strict) energy $\Delta E_1$, in the composite $B_1S_1$, and the change in energy $\Delta E_2$, in the composite $B_2S_2$, are related as

$$\beta_1 \Delta E_1 + \beta_2 \Delta E_2 = 0.$$  

(C9)

Therefore, the $\beta_1$ and $\beta_2$ are the quantities that determine the rate of energy exchange between $B_1S_1$ and $B_2S_2$ composites.

As a remark, we note that the semi-local thermal operations, in Definition 7, are capable of changing the system Hamiltonians, and we consider one protocol to do so in Section F3.

1. **Catalytic semi-local thermal operations (cSLTOs)**

To capture the full structure of the thermodynamical interactions in the presence of two baths, we generalize the semi-local thermal operations to the cases where an additional system is used as a catalyst. These catalytic SLTOs (cSLTOs) are the extension of SLTOs, where a catalyst assists to implement an SLTO without changing itself before and after the operation.

Consider a system $S_{12}$, with Hamiltonian $H_{S_{12}} = H_{S_1} \otimes I_{S_2} + I_{S_1} \otimes H_{S_2}$, in a state $\rho_{S_{12}}$, a catalyst system $C_{12}$, with a Hamiltonian $H_{C_{12}} = H_{C_1} \otimes I_{C_2} + I_{C_1} \otimes H_{C_2}$, in a state $\rho_{C_{12}}$. Through an SLTO, the composite system $S_1C_1$ is semi-locally interacting with the bath $B_1$ at inverse temperature $\beta_1$, and similarly $S_2C_2$ is semi-locally interacting with the bath $B_2$ at inverse temperature $\beta_2$.

Then, the catalytic SLTO is defined as

$$\Lambda_{S_{12}C_{12}}(\rho_{S_{12}} \otimes \rho_{C_{12}}) = \sigma_{S_{12}} \otimes \rho_{C_{12}},$$  

(C10)

with the protocol described in Definition 7. Return of the catalyst in the same state and uncorrelated with the system enable us to re-use the catalyst for any other catalytic SLTO. In general, the cSLTOs form a larger set of engine operations than that of SLTOs.

**Appendix D: Characterization of semi-local thermal operations**

Recall the protocol (in Definition 7) to implement the SLTOs in Eq. (C5) with the condition on weighted-energy conservation by (C6). We stick to the non-interacting Hamiltonian of the system ($S_{12}$) as $H_{S_{12}} = H_{S_1} \otimes I + I \otimes H_{S_2}$. The baths, $B_1$ and $B_2$ with the Hamiltonians $H_{B_1}$ and $H_{B_2}$ respectively, are at thermal equilibrium with the inverse temperatures $\beta_1$ and $\beta_2$, where $\beta_1 < \beta_2$.

We exploit the framework which is developed in Section A 3 to characterize the SLTOs with slight modifications. The joint system-bath composite state is expressed in block-diagonal form corresponding to the unit-less quantities $E_{12}^{\beta_1} = \beta_1 E_1 + \beta_2 E_2$, which we term as the total weighted-energy. Here energies are $E_1 = E_{B_1} + E_{S_1}$, $E_2 = E_{B_2} + E_{S_2}$. With the projectors $\{P_{E_{12}^{\beta_1}}\}$, spanning the system-bath joint space with same value of total weighted-energies $E_{12}^{\beta_1}$, the joint system-bath state is expressed
as

\[ \gamma_{S_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}} = \sum_{E_{12}^{\beta_1 \beta_2}} P_{E_{12}^{\beta_1 \beta_2}} (\gamma_{S_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}}) P_{E_{12}^{\beta_1 \beta_2}}, \]  

(D1)

\[ = \sum_{E_{12}^{\beta_1 \beta_2}} P_{E_{12}^{\beta_1 \beta_2}} P_{E_{12}^{\beta_1 \beta_2}}. \]  

(D2)

The probability is \( P_{E_{12}^{\beta_1 \beta_2}} = \text{Tr} [P_{E_{12}^{\beta_1 \beta_2}} (\gamma_{S_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}})] \). Now for \( E_1, E_2 \in F_1 \) and \( E_2, E_2 \in F_2 \), the normalized state of the bath-system composites, in the total weighted-energy block \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \), is given by

\[ P_{E_{12}^{\beta_1 \beta_2}} = \sum_{E_{12}^{\beta_1 \beta_2}} \frac{1}{g_{B_1}(E_1)e^{-\beta_1 E_1}} \otimes \frac{1}{g_{B_2}(E_2)e^{-\beta_2 E_2}} \otimes P_{E_{12}^{\beta_1 \beta_2}} (\rho_{S_{12}}) P_{E_{12}^{\beta_1 \beta_2}}, \]  

(D3)

where \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \) is the system weighted-energy and \( P_{E_{12}^{\beta_1 \beta_2}} \) is the projector correspond to that system weighted-energy.

The unitary \( U_{BS} \), in Definition 7, strictly commutes with the total weighted-energy. Therefore, it can also be expressed in terms of the total weighted-energy blocks, as

\[ U_{BS} = \sum_{E_{12}^{\beta_1 \beta_2}} P_{E_{12}^{\beta_1 \beta_2}} (U_{BS}) P_{E_{12}^{\beta_1 \beta_2}} = \sum_{E_{12}^{\beta_1 \beta_2}} U_{BS}^{E_{12}^{\beta_1 \beta_2}}. \]  

(D4)

Note the unitary \( U_{BS}^{E_{12}^{\beta_1 \beta_2}} \) is only acting in the total weighted-energy block \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \) and could be an arbitrary unitary within the block, as it satisfies the constraint (C6). Further, the unitary \( U_{BS}^{E_{12}^{\beta_1 \beta_2}} \) cannot transfer populations among different total weighted-energy blocks.

### 1. SLTOs are those that preserve semi-Gibbs states, and vice versa

From the definition of SLTOs itself, it is clear that these operations preserve semi-Gibbs states. Let us consider the microscopic picture. Say the initial system state is in the semi-Gibbs state, given by

\[ \rho_{S_{12}} = \gamma_{S_1} \otimes \gamma_{S_2} = \sum_i e^{-\beta_i E_i^S} |E_i^S_1 \rangle \langle E_i^S_1| \otimes \sum_j e^{-\beta_j E_j^S} |E_j^S_2 \rangle \langle E_j^S_2|, \]  

(D5)

where \( |E_i^{S_{1/2}} \rangle \) are the energy eigenstates of the Hamiltonians \( H_{S_{1/2}} = \sum_{i,j} E_{i,j}^{S_{1/2}} |E_{i,j}^{S_{1/2}} \rangle \langle E_{i,j}^{S_{1/2}}| \) of the subsystems \( S_{1/2} \). The \( Z_{S_{1/2}} \) are the partition functions. For each block with the total weighted-energy \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \), the bath-system composite state, as in Eq. (D3), is

\[ \rho_{E_{12}^{\beta_1 \beta_2}} = \sum_{E_{12}^{\beta_1 \beta_2}} \frac{1}{g_{B_1}(E_1)e^{-\beta_1 E_1}} \otimes \frac{1}{g_{B_2}(E_2)e^{-\beta_2 E_2}} \otimes \left( e^{-\beta_i E_i^S_1} |E_i^S_1 \rangle \langle E_i^S_1| \right) \otimes \left( e^{-\beta_j E_j^S_2} |E_j^S_2 \rangle \langle E_j^S_2| \right), \]  

(D6)

\[ = \frac{1}{g_{B_1}(E_1)Z_{S_1}} \otimes \frac{1}{g_{B_2}(E_2)Z_{S_2}}. \]  

(D7)

Clearly, the application of a strict total weighted-energy conserving unitary, with the form (D4), on the joint system-bath composite will not change the maximally mixed state (D7) in every weighted-energy block. Therefore, a semi-Gibbs state will not change upon the application of an SLTO. Now we consider the reverse statement, placed in the Corollary below.

**Corollary 8** (Semi-Gibbs preservation of semi-local thermal operations). Consider two non-interacting sub-systems \( S_1 \) and \( S_2 \), of a bipartite system \( S_{12} \), that are semi-locally interacting with the baths \( B_1 \) and \( B_2 \), at inverse temperatures \( \beta_1 \) and \( \beta_2 \), respectively. Then the semi-local thermal operations are the ones that satisfy the semi-Gibbs preservation condition,

\[ A_{S_{12}} (\gamma_{S_1} \otimes \gamma_{S_2}) = \gamma'_{S_1} \otimes \gamma'_{S_2} \in T_{S_{12}}, \quad \forall \gamma_{S_1} \otimes \gamma_{S_2} \in T_{S_{12}}. \]  

(D8)
Proof. Let us just consider the situation where the Hamiltonians of the sub-systems do not change, i.e., the situation where \( \mathcal{A}_{S_{12}}(\gamma_S, \otimes \gamma_S) = \gamma_S, \otimes \gamma_S \). Extension to the general cases can be simply followed.

Below we show that the semi-Gibbs preserving operations are precisely the semi-local thermal operations given in Definition 7. Let us consider that the weighed Hamiltonian of the system,

\[
H_{S_{12}}^{\beta_1 \beta_2} = \beta_1 H_{S_1} \otimes 1 + 1 \otimes \beta_2 H_{S_2},
\]

is non-degenerate in system weighted-energy. The bath-system composite \( (B_1B_2S_{12}) \) in the total weighted-energy blocks \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \) is expressed in Eq. (D3). We restrict ourselves within one total weighted-energy block \( E_{12}^{\beta_1 \beta_2} \). We show that, with the help of just permutation between bases, any arbitrary operation can be performed that preserves the corresponding semi-Gibbs state within the total weighted-energy block. Once done with this, it will be easy to check that such an operation can be implemented in every weighted-energy block \( E_{12}^{\beta_1 \beta_2} \), where \( E_1 \in \mathcal{E}_1 \) and \( E_2 \in \mathcal{E}_2 \). The permutations among the bases will result in transfer of bases among the sub-blocks defined by \( \beta_1 E_1^{S_1} + \beta_2 E_2^{S_2} \) (the weighted-energy of the system).

Within a block of total weighted-energy \( E_{12}^{\beta_1 \beta_2} = \beta_1 E_1 + \beta_2 E_2 \), there are sub-blocks corresponding to the system weighted-energies defined by \( \beta_1 E_1^{S_1} + \beta_2 E_2^{S_2} \). Each sub-block also constitutes a degenerate subspace with the dimension \( g_{\beta_1}(E_1)e^{-\beta_1 E_1^{S_1}}g_{\beta_2}(E_2)e^{-\beta_2 E_2^{S_2}} \) (see Eq. (D3)). All the eigenvalues of the system-bath composite in this sub-block become equal to

\[
\frac{p(\beta_1 E_1^{S_1} + \beta_2 E_2^{S_2})}{g_{\beta_1}(E_1)e^{-\beta_1 E_1^{S_1}}g_{\beta_2}(E_2)e^{-\beta_2 E_2^{S_2}}},
\]

after normalization, where \( p(\beta_1 E_1^{S_1} + \beta_2 E_2^{S_2}) = \text{Tr}[P_{\beta_1 E_1^{S_1} + \beta_2 E_2^{S_2}} \rho_{S_{12}}] \). For the notational simplicity, let us denote \( p(\beta_1 E_1^{S_1} + \beta_2 E_2^{S_2}) \rightarrow p_{ij} \), where \( i \) (and \( j \)) stands for the energy levels \( E_1^{S_1} \) in system \( S_1 \) (and \( E_2^{S_2} \) in system \( S_2 \)), and \( g_{\beta_1}(E_1)e^{-\beta_1 E_1^{S_1}} \rightarrow d_i \) and \( g_{\beta_2}(E_2)e^{-\beta_2 E_2^{S_2}} \rightarrow d_j \). Then, due to permutations within the same total weighted-energy eigenstates, the 'transition currents' between system weighted-energy sub-blocks is denoted by \( t_{ij \rightarrow mn} \), which is equal to the number of eigenstates that are transferred from the \( ij \)-th sub-block (correspond to the system weighted-energy \( \beta_1 E_1^{S_1} + \beta_2 E_2^{S_2} \)) to \( mn \)-th sub-block (correspond to the system weighted-energy \( \beta_1 E_1^{S_1} + \beta_2 E_2^{S_2} \)). The transition current satisfies

\[
\sum_{ij} t_{ij \rightarrow mn} = d_m d_n,
\]

\[
\sum_{mn} t_{ij \rightarrow mn} = d_i d_j.
\]

The permutations will lead to a modification in the probability distribution in the system part \( \{p_{ij}\} \rightarrow \{q_{mn}\} \). The new probability distribution can be written in terms of the transition currents, satisfying (D11) and (D12), becomes

\[
q_{mn} = \sum_{ij} t_{ij \rightarrow mn} \frac{p_{ij}}{d_i d_j} = \sum_{ij} s_{ij \rightarrow mn} p_{ij},
\]

where \( s_{ij \rightarrow mn} = \frac{t_{ij \rightarrow mn}}{d_j} \) is the probability of the transition \( ij \rightarrow mn \). The transition matrix \( \{s_{ij \rightarrow mn}\} \) transforms a normalized probability distribution to another normalized probability distribution, as it satisfies the stochastic condition \( \sum_{mn} s_{ij \rightarrow mn} = 1, \forall j \).

Along with the relation \( \frac{dd_i}{d_m} \), the stochastic condition implies that all transformations satisfying the constraints (D11) and (D12) guarantee the preservation of the semi-Gibbs state \( \gamma_S, \otimes \gamma_S \). With this, we prove that in a given total weighted-energy block, all possible operations are semi-Gibbs preserving operations.

Note, for a given arbitrary semi-Gibbs preserving transformation on the system \( S_{12} \) in a state \( \rho_{S_{12}} \), a permutation among the system weighted-energy sub-blocks within a fixed total weighted-energy block, can be performed to result in the desired transformation. Since the permutations are restricted to each total weighted-energy block, the operations are strictly total weighted-energy conserving. Further for every total weighted-energy block, there exists permutation operation that leads to the same transformation on the part of the system \( S_{12} \). The combination of all these individual transformations, that are performed in all the different total weighted-energy blocks, leads to the implementation of the semi-Gibbs preserving operation on the initial state of the system \( S_{12} \).

It is clear from above that all semi-Gibbs preserving transformations can be performed with the help of permutations in each total weighted-energy block. Again, these are strictly weighted-energy preserving operations. The semi-local thermal operations (given in Definition 7) are also semi-Gibbs preserving operations (discussed above). Therefore, arbitrary semi-local thermal operations can be implemented using the same transformations.

\[ \square \]
We shall re-consider this semi-Gibbs preserving property to characterize the state transformations under SLTOs in Section F 1, and in the context of majorization in the Theorem 14.

2. Time-translation symmetry of semi-local thermal operations

Let us now examine the time-translation symmetry of the semi-local thermal operations given in the Definition 7. We may rewrite the operations as \( \Lambda_{S_{12}} (\rho_{S_{12}}) = \text{Tr}_{B_1}\text{Tr}_{B_2} \left[U (\gamma_{B_1} \otimes \gamma_{B_2} \otimes \rho_{S_{12}}) U^\dagger \right] \), with the condition that the global unitary commutes with the weighted Hamiltonians as

\[
\left[ U, H^{\beta_{B_2}}_{S_{12}} \otimes I + I \otimes H^{\beta_{B_2}}_{S_{12}} \right] = 0,
\]

where \( H^{\beta_{B_2}}_{S_{12}} = \beta_1 H_{S_1} \otimes I + I \otimes \beta_2 H_{S_2} \) is the weighted Hamiltonian of the system and \( H^{\beta_{B_2}}_{B_{12}} = \beta_1 H_{B_1} \otimes I + I \otimes \beta_2 H_{B_2} \) is the weighted Hamiltonian of the baths.

Now it is easy to see that the SLTOs are time-translation symmetric with respect to the generator \( H^{\beta_{B_2}}_{S_{12}} \), as well as with respect to the local sub-system Hamiltonians \( H_{S_1} \) and \( H_{S_2} \). Mathematically it means, \( \forall t \) and \( \forall \rho_{S_{12}} \),

\[
\Lambda_{S_{12}} e^{-itH_{S_{12}} \rho_{S_{12}} e^{itH_{S_{12}}}} = e^{-itH_{S_{12}} \Lambda_{S_{12}} (\rho_{S_{12}}) e^{itH_{S_{12}}}},
\]

and

\[
\Lambda_{S_{12}} e^{-iH_{B_{12}} \rho_{S_{12}} e^{iH_{B_{12}}}} = e^{-iH_{B_{12}} \Lambda_{S_{12}} (\rho_{S_{12}}) e^{iH_{B_{12}}}},
\]

Clearly the Eqs. (15), (16) and (17) imply that the SLTOs commute with the dephasing operations in the eigenbases of the weighted Hamiltonian of the system \( H^{\beta_{B_2}}_{S_{12}} = \beta_1 H_{S_1} \otimes I + I \otimes \beta_2 H_{S_2} = \sum_i \beta_1 E^{i1} + \beta_2 E^{i2} \otimes |i \rangle \langle j| \), and the sub-system Hamiltonians \( H_{S_1} = \sum_i E_i^{S_1} |i \rangle \langle i| \) and \( H_{S_2} = \sum_j E_j^{S_2} |j \rangle \langle j| \), i.e.,

\[
\Lambda_{S_{12}} \circ D^{\beta_{B_2}}_{S_{12}} = D^{\beta_{B_2}}_{S_{12}} \circ \Lambda_{S_{12}},
\]

\[
\Lambda_{S_{12}} \circ (D_{S_1} \otimes D_{S_2}) = (D_{S_1} \otimes D_{S_2}) \circ \Lambda_{S_{12}},
\]

where \( D^{\beta_{B_2}}_{S_{12}} \) and \( D_{S_1} \otimes D_{S_2} \) are the dephasing operations. These operations can be achieved by averaging over time-translations for a long enough time \( T \),

\[
D^{\beta_{B_2}}_{S_{12}} (\rho_{S_{12}}) = \frac{1}{T} \int_0^T e^{-itH_{B_{12}} \rho_{S_{12}} e^{itH_{B_{12}}}} dt,
\]

\[
D_x (\rho_x) = \frac{1}{T} \int_0^T e^{-itH_x \rho_x e^{itH_x}} dt, \quad \text{for } x = 1, 2.
\]

The Eq. (18) signifies that the diagonal elements in the eigenbases of \( H^{\beta_{B_2}}_{S_{12}} \), i.e., \( D^{\beta_{B_2}}_{S_{12}} (\rho_{S_{12}}) \), evolve independently of the off-diagonal elements. Similarly, the Eq. (19) signifies that block-diagonal elements of \( \rho_{S_{12}} \) in the local energy eigenbases, i.e., \( D_{S_1} \otimes D_{S_2} (\rho_{S_{12}}) \), evolve independently of its off-diagonal elements under SLTOs. We shall use these properties to formulate and supplement the second laws for state transformations later.

Appendix E: Information theoretic notations and technical tools

In this section, we shall briefly outline the notations and tools that will be used to derive the conditions of state transformation under SLTOs. The interested readers are referred to [8, 10] for more details.

1. Rényi \( \alpha \)-entropies

Given an \( k \)-dimensional probability distribution \( p = \{ p_i \}_{i=1}^k \), the Rényi \( \alpha \)-entropies are defined as

\[
H_\alpha (p) = \frac{\text{sgn}(\alpha)}{1 - \alpha} \log \sum_{i=1}^k p_i^\alpha, \quad \forall \alpha \in \mathbb{R} \setminus \{0, 1\},
\]

(E1)
where \( \text{sgn}(\alpha) = 1 \) for \( \alpha \geq 0 \) and \( \text{sgn}(\alpha) = -1 \) for \( \alpha < 0 \). For \( \alpha \in [-\infty, 0, 1, \infty) \), the \( H_\alpha \)s can be computed using limits, and they are

\[
H_\infty(p) = \log p_{\min}, \quad H_0(p) = \log \text{rank}(p), \quad H_1(p) = -\sum_{i=1}^{k} p_i \log p_i, \quad \text{and} \quad H_\infty(p) = -\log p_{\max}.
\]

(E2)

The rank\((p)\) means the number of non-zero elements in \( p \), and \( p_{\min} \) and \( p_{\max} \) are the elements with smallest and largest values in \( p \).

These Rényi entropies can also be defined for arbitrary quantum state \( \rho \), where the \( \{p_i\} \) would be the eigenvalues of the density matrix \( \rho \). Note, at \( \alpha \to 1 \), the \( H_1(p) = -\text{Tr} \rho \log \rho \) becomes the von Neumann entropy of the state \( \rho \).

2. Rényi \( \alpha \)-relative entropies

For any two \( k \)-dimensional probability distributions \( p = \{p_i\}_{i=1}^k \) and \( q = \{q_i\}_{i=1}^k \), the Rényi \( \alpha \)-relative entropies are defined as

\[
D_\alpha(p \parallel q) = \frac{\text{sgn}(\alpha)}{\alpha - 1} \log \sum_{i=1}^{k} p_i^{\alpha} q_i^{1-\alpha}, \quad \forall \alpha \in [-\infty, \infty].
\]

(E3)

For the cases \( \alpha \in [-\infty, 0, 1, \infty) \), the \( D_\alpha \)s are calculated using limits, as

\[
D_\infty(p \parallel q) = \lim_{\alpha \to \infty} D_\alpha(p \parallel q) = \log \max_i q_i,
\]

(E4)

\[
D_{-\infty}(p \parallel q) = \lim_{\alpha \to -\infty} D_\alpha(p \parallel q) = D_\infty(q \parallel p),
\]

(E5)

\[
D_0(p \parallel q) = \lim_{\alpha \to 0^+} D_\alpha(p \parallel q) = -\log \sum_{i:p_i \neq 0} q_i,
\]

(E6)

\[
D_1(p \parallel q) = \lim_{\alpha \to 1} D_\alpha(p \parallel q) = \sum_i p_i (\log p_i - \log q_i).
\]

(E7)

Here we use the conventions that \( \frac{0}{0} = 0 \) and \( \frac{\infty}{\infty} = \infty \) for \( x > 0 \). The Rényi \( \alpha \)-relative entropies satisfy many interesting properties, and we shall mention few useful ones below. These entropies monotonically decrease under stochastic maps \( \Lambda \), i.e.,

\[
D_\alpha(p \parallel q) \geq D_\alpha(\Lambda(p) \parallel \Lambda(q)), \quad \forall \alpha \in [-\infty, \infty].
\]

(E8)

The inequalities are also known as the data-processing inequality. Another important property is that, for \( \alpha \in [0, \infty) \),

\[
D_\alpha(p \parallel q) \leq D_\alpha(p \parallel q), \quad \text{for} \quad \alpha \leq \delta.
\]

(E9)

For a \( k \)-dimensional probability distribution \( \{q_i\}_{i=1}^k \) with \( 0 < q_i < 1 \) and \( \forall q_i \in \mathbb{Q} \), there exist a set of natural numbers \( \{d_i\}_{i=1}^k \) such that \( \sum_i d_i = N \) and \( q_i = \frac{d_i}{N} \). Then a fine-grained, \( N \)-dimensional uniform probability can be written as

\[
\Gamma(q) = \left\{ \frac{q_1}{d_1}, \cdots, \frac{q_1}{d_1}, \frac{q_k}{d_k}, \cdots, \frac{q_k}{d_k} \right\} = \left\{ \frac{1}{N}, \cdots, \frac{1}{N} \right\}.
\]

(E10)

Similarly, any other probability distribution \( \{p_i\}_{i=1}^k \) can be fine grained to

\[
\Gamma(p) = \left\{ \frac{p_1}{d_1}, \cdots, \frac{p_1}{d_1}, \frac{p_k}{d_k}, \cdots, \frac{p_k}{d_k} \right\}.
\]

(E11)

Then, for \( \alpha \in [-\infty, \infty] \), the Rényi \( \alpha \)-relative entropies are related to the Rényi \( \alpha \)-entropies as

\[
D_\alpha(p \parallel q) = D_\alpha(\Gamma(p) \parallel \Gamma(q)) = \text{sgn}(\alpha) \log N - H_\alpha(p).
\]

(E12)

For the situations where \( q_i \notin \mathbb{Q} \), we can relate the Rényi \( \alpha \)-relative entropies with the Rényi \( \alpha \)-entropies using following Lemma.
Lemma 9 (Ref. [10]). Consider a non-increasingly ordered, k-dimensional probability distribution \( q = \{ q_i \}_{i=1}^k \) with \( \forall q_i > 0 \), and \( q_i \)'s may possibly assume irrational values. Then, for any \( \epsilon > 0 \), there exists a probability distribution \( q_\epsilon \) such that

(i) \( \| q - q_\epsilon \| < \epsilon \),

(ii) Each probability in \( q_\epsilon \) is rational so that \( q_\epsilon = \{ \frac{d_i}{N} \}_{i=1}^k \), where \( \forall d_i \in \mathbb{N} \) and \( \sum_{i=1}^k d_i = N \).

(iii) There exists a stochastic channel \( \Lambda \) such that \( \Lambda(q) = q_\epsilon \), and for any arbitrary probability distribution \( r \), the channel satisfies \( \| r - \Lambda(r) \| \leq O(\sqrt{\epsilon}) \).

The Rényi \( \alpha \)-relative entropies can be extended to two arbitrary quantum states \( \rho \) and \( \sigma \). For this work, we shall restrict to the cases where \( [\rho, \sigma] = 0 \), and \( \text{supp}[\rho] \subseteq \text{supp}[\sigma] \). Then the Rényi \( \alpha \)-relative entropies are defined as

\[
D_\alpha(\rho \parallel \sigma) = \frac{\text{sgn}(\alpha)}{\alpha - 1} \log \Tr[\rho^\alpha \sigma^{1-\alpha}], \quad \forall \alpha \in [-\infty, \infty].
\] (E13)

For \( \alpha \to 0 \), it becomes the min-relative entropy,

\[
D_{\text{min}}(\rho \parallel \sigma) = D_0(\rho \parallel \sigma) = -\log \Tr[\Pi_\rho \sigma],
\] (E14)

where \( \Pi_\rho \) is the projector onto the support of the state \( \rho \). For the \( \alpha \to 1 \), it reduces to the von Neumann relative entropy as

\[
D_1(\rho \parallel \sigma) = \Tr[\rho \log \rho - \log \sigma].
\] (E15)

For the case \( \alpha \to \infty \), it results in the max-entropy given by

\[
D_{\text{max}}(\rho \parallel \sigma) = D_{\infty}(\rho \parallel \sigma) = \log \min\{\lambda : \rho \leq \lambda \sigma\}.
\] (E16)

The Rényi \( \alpha \)-relative entropies are known to satisfy the monotonicity relation under completely positive maps, for \( \alpha \in [0, 2] \),

\[
D_\alpha(\rho \parallel \sigma) \geq D_\alpha(\Lambda(\rho) \parallel \Lambda(\sigma)).
\] (E17)

For other values of \( \alpha \), validity of the monotonicity is still an open question.

3. Majorization and catalytic majorization (tramping)

The majorization relations are useful to introduce partial orders between arbitrary probability distributions [31]. For any two probability distributions \( p = \{ p_i \}_{i=1}^k \) and \( p' = \{ p'_i \}_{i=1}^k \), we say that \( p \) majorizes \( p' \), i.e., \( p \succ p' \), if for all \( l = 1, \ldots, k \),

\[
\sum_{i=1}^l p_i^l \geq \sum_{i=1}^l p'_i^l \quad \text{and} \quad \sum_{i=1}^k p_i^l = \sum_{i=1}^k p'_i^l = 1,
\] (E18)

where the \( p_i^l \) is obtained by rearranging \( p \) in the non-increasing order so that \( p_1^l \geq p_2^l \geq \ldots \geq p_k^l \), and similarly we obtain \( p'_i^l \) by rearranging \( p' \). When two probability distributions are partially ordered through a majorization relation, these satisfy the following properties:

(i) Two probability distributions \( p \) and \( p' \) satisfy a majorization relation, \( p \succ p' \) if and only if there exist a channel \( \Lambda \) such that \( p' = \Lambda(p) \) and \( \Lambda \) satisfies \( \Lambda(\eta) = \eta \), where \( \eta \) is the uniform distribution. The channels \( \Lambda \) are called bi-stochastic channels, and these can be implemented using random unitary operations.

(ii) If two probability distributions \( p \) and \( p' \) satisfy a majorization relation, \( p \succ p' \), then

\[
f(p) \leq f(p'),
\] (E19)

where \( f \) are all Schur-concave functions. Note, the Rényi \( \alpha \)-entropies \( H_\alpha \) are Schur-concave functions for \( \alpha \in [-\infty, \infty] \).

Let us now discuss catalytic majorization or tramping. There are situations where \( p \) and \( p' \) cannot be partially ordered in terms of majorization, but in presence of an additional probability distribution \( x \), it satisfies \( p \otimes x \succ p' \otimes x \). This is termed as “\( p \) tramps \( p' \)" or \( p \succ_T p' \). For two given probability distribution it is often very difficult to find the additional probability distribution \( x \) to check if the formers are related through tramping. However, if the two probability distributions satisfy following two Lemmas, then one could ensure the existence of at least one \( x \).

Lemma 10 (Ref. [10]). Let us consider two probability distributions \( p \) and \( p' \) that do not contain any element equal to zero. Then, \( p \) tramps \( p' \), i.e., \( p \succ_T p' \) if, and only if, the Rényi \( \alpha \)-entropies satisfy

\[
H_\alpha(p) \leq H_\alpha(p'), \quad \forall \alpha \in (-\infty, \infty).
\] (E20)
Obviously, there are situations where the $p$ and $p'$ are not of full-ranks (i.e., with all non-zero elements). In this situation, the Lemma below holds.

**Lemma 11** (Ref. [10]). Let us consider two arbitrary probability distributions $p$ and $p'$. Then the following are equivalent:

(i) For an arbitrary $\epsilon > 0$, there exists a full rank probability distribution $p'_\epsilon$ such that $\| p' - p'_\epsilon \| \leq \epsilon$ and $p$ tramps $p'_\epsilon$ (i.e., $p \geq_T p'_\epsilon$). (ii) The inequalities are satisfied, $H_\alpha(p) \leq H_\alpha(p')$, $\forall \alpha \in (-\infty, \infty)$.

The notion of majorization and tramping can also be extended to quantum states, say between $\rho$ and $\rho'$. Then, the majorization relation $\rho \geq \rho'$ implies the relations (E18) where the $p^\dagger$ and $p'^\dagger$ are the non-increasingly ordered eigenvalues of $\rho$ and $\rho'$ respectively.

4. $d$-majorization and catalytic $d$-majorization

Not only for two probability distributions, but the majorization-like partial ordering can also be drawn between two pairs of probability distributions. Consider two pairs of probability distributions $(p, q)$ and $(p', q')$. The $(p, q)$ $d$-majorizes $(p', q')$ if and only if

$$\sum_i q_i f \left( \frac{p_i}{q_i} \right) \leq \sum_i q'_i f \left( \frac{p'_i}{q'_i} \right),$$

(E21)

for any arbitrary concave function $f$. This $d$-majorization based pre-ordering is then denoted as $d(p,q) \geq d(p',q')$. Given this definition of $d$-majorization, we present the following Lemma.

**Lemma 12** (Ref. [10]). Let us consider four probability distributions $p, p', q, and q'$. Then the following statements are equivalent:

(i) The pair $(p, q)$ $d$-majorizes the pair $(p', q')$, i.e., $d(p,q) \geq d(p',q')$. (ii) There exists a stochastic channel $\Lambda$ that satisfies $\Lambda(p) = p'$ and $\Lambda(q) = q'$.

A catalytic $d$-majorization can also be introduced as in the following.

**Lemma 13** (Ref. [10]). For two pairs of probability distributions, $(p, q)$ and $(p', q')$ with the constraints that $q$ and $q'$ are of full rank, the following conditions are equivalent:

(i) The Rényi $a$-relative entropies satisfy $D_a(p \parallel q) \geq D_a(p' \parallel q')$, $\forall a \in [-\infty, \infty]$.

(ii) For $\epsilon > 0$, there exists full-rank probability distributions $r, s,$ and $p'_\epsilon,$ and a stochastic channel $\Lambda$ such that

(a) $\Lambda(p \otimes r) = p'_\epsilon \otimes r$,

(b) $\Lambda(q \otimes s) = q' \otimes s,$ moreover $s$ can be a uniform distribution $\eta$ onto the support of $r$,

(c) $\| p' - p'_\epsilon \| \leq \epsilon$.

We shall use this Lemma for the derivations of the second laws for the state transformations under cSLTOs.

**Appendix F: Second laws for transformations between states block-diagonal in weighted-energy**

In this section, we present the necessary and sufficient conditions for state transformations, i.e., the second laws of state transformations, under (catalytic) semi-local thermal operations. All the necessary and sufficient conditions derived here are based on the assumption that the initial states are block-diagonal in weighted-energy eigenbases of the weighted Hamiltonian $H_{S_{12}}^{\alpha;\beta_1;\beta_2} = \beta_1 H_{S_1} \otimes 1 + 1 \otimes \beta_2 H_{S_2}$. However, the conditions still apply to initial non-block-diagonal states, but only as the necessary conditions.

We start with a bipartite system $S_{12}$, with non-interacting Hamiltonian $H_{S_{12}} = H_{S_1} \otimes I_{S_2} + I_{S_1} \otimes H_{S_2}$, and the initial state $\rho_{S_{12}}$. The subsystem $S_1$ ($S_2$) is semi-locally interacting with a bath $B_1$ ($B_2$) at inverse temperature $\beta_1$ ($\beta_2$). After a transformation, the final state of the system becomes $\sigma_{S_{12}}$. At this stage, we assume that the system Hamiltonian remain unchanged before and after the transformation. Our goal is to find necessary and sufficient conditions with which we can ascertain that the transformation

$$(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma_{S_{12}}, H_{S_{12}})$$

is possible via a semi-local thermal operation $\Lambda$, and vice versa.
1. State transformation in absence of a catalyst

Suppose, we do not have access to a catalyst. Following the discussion made in Sections A.3 and D, we rewrite the initial system-bath composite as

$$\gamma_B \otimes \gamma_B \otimes \rho_{S_{12}} = \sum_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}} \left( \gamma_B \otimes \gamma_B \otimes \rho_{S_{12}} \right) P_{E_{12}^{\beta_1\beta_2}},$$

(E2)

$$= \sum_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{B_{12} S_{12}}},$$

(F3)

Here the projector $P_{E_{12}^{\beta_1\beta_2}}$ spans the system-bath joint space with the same value of total weighted-energy $E_{12}^{\beta_1\beta_2}$. The probabilities $P_{E_{12}^{\beta_1\beta_2}} = \text{Tr} \left( P_{E_{12}^{\beta_1\beta_2}} \left( \gamma_B \otimes \gamma_B \otimes \rho_{S_{12}} \right) \right)$. Now for $E_1, E_{B_1} \in E_1$ and $E_2, E_{B_2} \in E_2$, the normalized state of the bath-system composites, in a total weighted-energy blocks $E_{12}^{\beta_1\beta_2} = \beta_1 E_1 + \beta_2 E_2$, is given by

$$P_{E_{12}^{B_{12} S_{12}}} = \frac{1}{g_{B_1}(E_1)e^{-\beta_1 E_1}} \otimes \frac{1}{g_{B_2}(E_2)e^{-\beta_2 E_2}} \otimes P_{E_{12}^{\beta_1\beta_2}}(\rho_{S_{12}})P_{E_{12}^{\beta_1\beta_2}},$$

(F4)

$$= \sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} \otimes P_{E_{12}^{\beta_1\beta_2}}(\rho_{S_{12}})P_{E_{12}^{\beta_1\beta_2}},$$

(F5)

where $E_{S_{12}}^{\beta_1\beta_2} = \beta_1 E_1 + \beta_2 E_2$ is the system weighted-energy and $P_{E_{12}^{\beta_1\beta_2}}$ is the projector correspond to the system weighted-energy $E_{S_{12}}^{\beta_1\beta_2} = \beta_1 E_1 + \beta_2 E_2$.

Similarly, the final joint state of the bath and the system composite can be expressed as

$$\gamma_B \otimes \gamma_B \otimes \rho_{S_{12}} = \sum_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}} \left( \gamma_B \otimes \gamma_B \otimes \sigma_{S_{12}} \right) P_{E_{12}^{\beta_1\beta_2}},$$

(F6)

$$= \sum_{E_{12}^{\beta_1\beta_2}} q_{E_{12}^{\beta_1\beta_2}} \sigma_{E_{12}^{\beta_1\beta_2}},$$

(F7)

where $q_{E_{12}^{\beta_1\beta_2}} = \text{Tr} \left( P_{E_{12}^{\beta_1\beta_2}} \left( \gamma_B \otimes \gamma_B \otimes \sigma_{S_{12}} \right) \right)$. For a total weighted-energy $E_{12}^{\beta_1\beta_2}$ block, the normalized state becomes

$$\sigma_{E_{12}^{\beta_1\beta_2}} = \sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} \otimes P_{E_{12}^{\beta_1\beta_2}}(\sigma_{S_{12}})P_{E_{12}^{\beta_1\beta_2}},$$

(F8)

With these structures of the initial and final states of the system-bath composites, we put forward the necessary and sufficient conditions for the transformations of block-diagonal states, under semi-local thermal operations.

a. Majorization condition

The conditions are derived in terms of majorization (see Section E.3) in the following theorem.

**Theorem 14** (Majorization condition for state transformations). Consider two states $\rho_{S_{12}}$ and $\sigma_{S_{12}}$ that are block-diagonal in the eigenbases of the weighted Hamiltonian of the system $H_{S_{12}}^{\beta_1\beta_2} = \beta_1 H_{S_1} \otimes \mathbb{1} + \mathbb{1} \otimes \beta_2 H_{S_2}$. Then the transformation $(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma_{S_{12}}, H_{S_{12}})$, by means of semi-local thermal operation, is possible if, and only if, the initial and final states of the system-bath composites satisfy the majorization relation

$$\sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}}(\rho_{S_{12}})P_{E_{12}^{\beta_1\beta_2}} \succ \sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}}(\sigma_{S_{12}})P_{E_{12}^{\beta_1\beta_2}},$$

(F9)

for large enough $E_1$ and $E_2$.

Moreover, for the cases where the initial system state is not block-diagonal in the eigenbases of $H_{S_{12}}^{\beta_1\beta_2}$, the necessary condition for the transformation $(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma_{S_{12}}, H_{S_{12}})$ is

$$\sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}}(\rho_{S_{12}})P_{E_{12}^{\beta_1\beta_2}} \succ \sum_{E_{12}^{\beta_1\beta_2}} \eta_{E_{12}^{\beta_1\beta_2}} P_{E_{12}^{\beta_1\beta_2}}(\sigma_{S_{12}})P_{E_{12}^{\beta_1\beta_2}},$$

(F10)
Proof. In the system-bath composite state, for a given total weighted-energy $E_{12}^{\beta_1\beta_2} = \beta_1 E_1 + \beta_2 E_2$, the allowed operations are the arbitrary unitary operations on the degenerate subspace. Because, an arbitrary unitary operation does not alter the total weighted-energy of the block. However, as we shall show below, we not only can apply arbitrary unitary operations but also implement arbitrary random unitary operations as long as we remain in this fixed total weighted-energy block. Note these are the only possible operations that are allowed on the systems-baths joint space as they strictly conserve the total weighted-energy.

We start with the first part of the theorem and prove it using a protocol involving the following steps, where the initial state of the system-bath composite is with total weighted-energy $E_{12}^{\beta_1\beta_2}$:

(i) Implementing random unitary operations: We assume that the $E_1$ and the $E_2$, corresponding to the weighted-energy $E_{12}^{\beta_1\beta_2}$, are reasonably large. This in turn implies that the dimension of the maximally mixed state $\eta_{E_{12}^{\beta_1\beta_2}}$ is exponentially large. Therefore we can divide the state in two normalized sub-parts, as

$$\eta_{E_{12}^{\beta_1\beta_2}} = \eta_{E_1^{\beta_1}} \otimes \eta_{E_2^{\beta_2}}$$

where each of the sub-parts are in maximally mixed states, and also with exponentially large dimensions. We further assume that $\eta_{E_{12}^{\beta_1\beta_2}}$ is so large that it hardly differ from $\eta_{E_{12}^{\beta_1\beta_2}}$. The initial state of the system-bath composite, with total weighted-energy $E_{12}^{\beta_1\beta_2}$, is then

$$\eta_{E_{12}^{\beta_1\beta_2}} = \bigoplus_{E_1^{\beta_1}} \bigoplus_{E_2^{\beta_2}} \bigoplus_{E_{12}^{\beta_1\beta_2}} P_{E_1^{\beta_1}}(\rho_{S_{12}})P_{E_2^{\beta_2}}(\rho_{S_{12}}).$$

Now, the state $\eta_{E_{12}^{\beta_1\beta_2}}$ can be used as a control state to implement arbitrary random unitary operations (i.e., a unital channel) on the rest of the system-bath composite, by using a global unitary on the entire system-bath composite. Let's say, we implement such a global unitary $U_{E_{12}^{\beta_1\beta_2}}$ (see Eq. (D4)) such that the resultant system state, after tracing out the baths, becomes $\sigma_{S_{12}}$. Note the joint state of the system-bath composite can still have correlations among them.

(ii) Destroying unwanted correlations in the system-bath composite state: Now, we can destroy the unnecessary correlations that may possibly present between the sub-systems and baths after (i). That is done by a “twirling” operation which is itself a random unitary operation within the weighted-energy block. For each system state with the weighted-energy $E_{12}^{\beta_1\beta_2} = \beta_1 E_1 + \beta_2 E_2$, we apply twirling operation on the bath part $B_1 B_2$ while applying identity operation on the system part, such that the transformed final system-bath state becomes classically correlated as

$$\bigoplus_{E_1^{\beta_1}} \bigoplus_{E_2^{\beta_2}} \bigoplus_{E_{12}^{\beta_1\beta_2}} P_{E_1^{\beta_1}}(\sigma_{S_{12}})P_{E_2^{\beta_2}}(\rho_{S_{12}}).$$

Both the operations applied in steps (i) and (ii) are random unitary operations, and these are the precursors of semi-local thermal operations in the joint space of systems and baths (see Section D). Further, if two states are related through random unitary operations, these states satisfy pre-ordering by a majorization relation, and this is a necessary and sufficient condition. Consequently, the transformation is possible if and only if the initial system-bath state majorizes the final one, with total weighted-energy $E_{12}^{\beta_1\beta_2}$. Now since baths are considerably large in energy compared to the systems, we can implement the random unitary operations, similar to the steps (i) and (ii), such that the reduced system state becomes exactly the same in each total weighted-energy block. As a result, we do not need to check the majorization relation for every total weighted-energy block. Therefore, the transition $(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma_{S_{12}}, H_{S_{12}})$ is possible if and only if the majorization relation (F9) is satisfied. With this, we complete the proof of the first part.

For the proof of the second part, we recall that the reduced operations on the system part, as the result of global unitary operations on the systems-baths composite, respect time-translation symmetry with respect to time translation by the weighted Hamiltonian of the system $H_{S_{12}}^{\beta_1\beta_2}$ (see Section D 2). The block-diagonal elements (also known as the ‘zero’ mode elements) of the system density matrix $(\rho_{S_{12}})$ with respect to the eigenbases of $H_{S_{12}}^{\beta_1\beta_2}$ evolve independently of the off-diagonal elements (‘non-zero’ modes) under this time-translation symmetric operations. Thus any transformation to happen between non-energy-block-diagonal initial and final state, it is necessary that the corresponding block-diagonal states must satisfy the majorization relation (F10). This relation cannot be sufficient condition as it does not encode information related to the off-diagonal elements. □

So far, we have derived the necessary and sufficient condition for transformations between block-diagonal states under semi-local thermal operations. However, the condition requires us a take into account both the system and the bath parameters simultaneously, which is not always practical.
Here we aim to derive a necessary and sufficient condition that exclusively depends on the system parameters, based on thermo-majorization. Consider two quantum states $\rho_{S_{12}}$ and $\sigma_{S_{12}}$, block-diagonal in the eigenbases of the weighted Hamiltonian $H_{12}^{\beta_1} = \beta_1 H_{S_1} \otimes \mathbb{1} + \mathbb{1} \otimes \beta_2 H_{S_2}$, with the probabilities $\{p_{ij}\}$ and $\{q_{ij}\}$ respectively. Here the weighted Hamiltonian of the system is written as $H_{12}^{\beta_1} = \sum_{ij} (\beta_1 E_{i1}^{0} + \beta_2 E_{j2}^{0}) |ij\rangle\langle ij|$, the probabilities are given by $p_{ij} = \langle ij|\rho_{S_{12}}|ij\rangle$ and $q_{ij} = \langle ij|\sigma_{S_{12}}|ij\rangle$. A pre-ordering is done by a non-increasing ordering of the quantities $\{p_{ij} e^{(\beta_1 E_{i1}^{0} + \beta_2 E_{j2}^{0})}\}$ and relabeled, so that

\[
p_{11} e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} \geq p_{12} e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} \geq p_{21} e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} \geq p_{22} e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} \geq \ldots.
\]

This determines the sequence in $\{p_{ij}\}$ which may or may not satisfy a non-decreasing order. We denote the set of the ordered probability distribution as $[p_{ij}]$, where $p_{11}$ is the $p_{ij}$ corresponding to the largest $p_{ij} e^{(\beta_1 E_{i1}^{0} + \beta_2 E_{j2}^{0})}$ value and so on. A similar pre-ordering is also done for $\{q_{ij}\} \rightarrow \{q_{ij}'\}$. Now we construct a Lorentz curve with the points correspond to the pairs

\[
\{(x, y) = ((0, 0), \\
(p_{11}, e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})}), \\
(p_{11} + p_{12}, e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})}), \\
(p_{11} + p_{12} + p_{21}, e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})}), \\
(p_{11} + p_{12} + p_{21} + p_{22}, e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})} + e^{(\beta_1 E_{11}^{0} + \beta_2 E_{22}^{0})}), \\
\ldots \\
(1, Z_{1} Z_{2})\}.
\]

Plotting these points gives a function $f_p(x)$, correspond to the state $\rho_{S_{12}}$. A similar function is also derived for $\{q_{ij}\}$, and that is $f_q(x)$ for $\sigma_{S_{12}}$.

**Theorem 15** (Thermo-majorization condition for state transformations). A transition $(\rho_{S_{12}}, H_{S_{12}}) \rightarrow (\sigma_{S_{12}}, H_{S_{12}})$ can occur under semi-local thermal operation if, and only if, the spectra of $\rho_{S_{12}}$ thermo-majorizes spectra of $\sigma_{S_{12}}$, i.e.,

\[
f_p(x) \geq f_q(x), \quad \forall x \in [0, Z_{1} Z_{2}].
\]

In this sub-section, the derived necessary and sufficient conditions based on majorization are very handy. This is in the sense that they are easy to check, in particular, the one based on thermo-majorization. However, as we have mentioned in Section E, there are probability distribution they do not satisfy majorization relation as such, but can still possess a majorization based pre-ordering by having access to another probability distribution as a catalyst. It is not easy to check whether there exists a probability distribution which can act as a catalyst. We can still find necessary and sufficient condition(s) based on Rényi relative entropies to ensure their existence, which we shall consider in the next sub-section.

### 2. Catalytic state transformation

Before we propose the necessary and sufficient conditions for the transformation under catalytic semi-local thermal operations, let us introduce the definition of $\alpha$-free-entropy ($S_\alpha$) in terms of the Rényi $\alpha$-relative entropy ($D_\alpha$).

#### a. $\alpha$-free-entropies

Consider a state $\rho_{S_{12}}$ of a bipartite system $S_{12}$ with Hamiltonian $H_{S_{12}} = H_{S_1} \otimes \mathbb{1} + \mathbb{1} \otimes H_{S_2}$, where the sub-system $S_1$ ($S_2$) is semi-locally interacting with the bath $B_1$ ($B_2$) at inverse temperature $\beta_1$ ($\beta_2$). Also, the state $\rho_{S_{12}}$ is block-diagonal in the eigenbases of the weighted Hamiltonian $H_{S_{12}}^{\beta_1 \beta_2}$. Then, the Rényi $\alpha$-relative entropy between the system state and its corresponding semi-Gibbs state, for $\alpha \in [-\infty, \infty]$, is given by

\[
D_\alpha(\rho_{S_{12}} \parallel \gamma_{S_1} \otimes \gamma_{S_2}) = \frac{\text{sgn}(\alpha)}{\alpha - 1} \log \text{Tr}[(\rho_{S_{12}})^{1-\alpha} (\gamma_{S_1} \otimes \gamma_{S_2})^{1-\alpha}],
\]
where the thermal states are \( \gamma_S = \frac{e^{-\beta H_S}}{Z} \), with \( Z = \text{Tr}[e^{-\beta H_S}] \) and \( i = 1, 2 \). Now the \( \alpha \)-free-entropy of the state \( \rho_{S_{12}} \) is defined as

\[
S_\alpha(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) = D_\alpha(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) - \log Z_1 Z_2, \quad \forall \alpha \in (-\infty, \infty].
\] (F17)

The name ’free-entropy’ is justified by fact that it quantifies the work potential stored in a system in terms of entropy, which we shall discuss in the Section H. For \( \alpha \to 1 \), the \( S_\alpha \) reduces to the Helmholtz free-entropy as

\[
S_1(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) = \beta_1 E_{S_1} + \beta_2 E_{S_2} - S(\rho_{S_{12}}),
\] (F18)

where \( S(\rho_{S_{12}}) = -\text{Tr} \rho_{S_{12}} \ln \rho_{S_{12}} \) is the von Neumann entropy and \( E_{S_i} = \text{Tr}[\rho_{S_i} H_{S_i}] \) is the average energy of the sub-system \( S_i \), with \( x = 1, 2 \). For the cases where the state \( \rho_{S_{12}} \) is uncorrelated, \( e_{12} = \rho_{S_1} \otimes \rho_{S_2} \), the \( \alpha \)-free-entropy becomes additive

\[
S_\alpha(\rho_{S_{12}}, \gamma_1 \otimes \gamma_2) = S_\alpha(\rho_{S_1}, \gamma_1) + S_\alpha(\rho_{S_2}, \gamma_2).
\]

### b. Second laws in terms of \( \alpha \)-free-entropies

Now with the notion of \( \alpha \)-free-entropy, we go on to propose the necessary and sufficient conditions for catalytic semi-local thermal operation, in the following theorem.

**Theorem 16.** Consider two states \( \rho_{S_{12}} \) and \( \sigma_{S_{12}} \) that are block-diagonal in the eigenstates of weighted Hamiltonian \( H_0^{\alpha_1} \), of a system with the non-interacting Hamiltonian \( H_{S_{12}} = H_S \otimes 1 + 1 \otimes H_{S_2} \). Then a transformation \( (\rho_{S_{12}}, H_{S_{12}}) \to (\sigma_{S_{12}}, H_{S_{12}}) \) is possible under semi-local thermal operation if, and only if, for all \( \alpha \in (-\infty, \infty) \),

\[
S_\alpha(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) \geq S_\alpha(\sigma_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2})
\] (F19)

**Remark:** The condition for \( \alpha = -\infty, \infty \) can be included by continuity.

**Proof.** Since the initial and final states are block-diagonal in weighted-energy eigenbases, the theorem above can be proved using catalytic \( d \)-majorization shown in the Lemma 13. Replacing the probability distributions, in Lemma 13, with the eigenvalues of the states block-diagonal in energy, as

- \( p \to \rho_{S_{12}} \): initial state of the system,
- \( p' \to \sigma_{S_{12}} \): final state of the system,
- \( q = q' \to \gamma_{S_1} \otimes \gamma_{S_2} \): semi-Gibbs state of the system,
- \( r \to \rho_{C_{12}} \): a catalyst
- \( s \to \gamma_{C_1} \otimes \gamma_{C_2} \): semi-Gibbs state of the catalyst.

Note, if we consider that the Hamiltonian of the catalyst \( H_{C_{12}} = H_{C_1} \otimes 1 + 1 \otimes H_{C_2} \) is trivial (i.e., \( H_{C_{12}} = 1 \)), then

\[
S = \gamma_{C_1} \otimes \gamma_{C_2} \to \eta: \text{ a uniform distribution}.
\]

Let us first assume that the catalyst possesses a trivial Hamiltonian \( H_{C_{12}} = 1 \) and the conditions (F19) are satisfied. The latter, in terms of Rényi \( \alpha \)-relative entropy, means

\[
D_\alpha(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) \geq D_\alpha(\sigma_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}), \quad \forall \alpha \in (-\infty, \infty).
\] (F20)

Then, as the Lemma 13 implies, there exists a catalyst \( \rho_{C_{12}} \) and a channel \( \Lambda \) that (i) preserves the semi-Gibbs state \( \gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{C_1} \otimes \gamma_{C_2} \), as

\[
\Lambda(\gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{C_1} \otimes \gamma_{C_2}) = \gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{C_1} \otimes \gamma_{C_2},
\] (F21)

and (ii) transforms the initial state as

\[
\Lambda(\rho_{S_{12}} \otimes \rho_{C_{12}}) = \rho_{S_{12}}^\alpha \otimes \rho_{C_{12}},
\] (F22)

where \( \| \rho_{S_{12}}^\alpha - \sigma_{S_{12}} \| \leq \epsilon \). As the operations that preserve semi-Gibbs states are also semi-local thermal operations (see Corollary 8), it implies that such a transformation using catalytic semi-local thermal transformation is possible.

Let us consider the converse now. Suppose there is a catalytic semi-local thermal channel \( \Lambda \) that transforms

\[
\Lambda(\rho_{S_{12}} \otimes \rho_{C_{12}}) = \rho_{S_{12}}^\beta \otimes \rho_{C_{12}},
\] (F23)

where \( \| \rho_{S_{12}}^\beta - \sigma_{S_{12}} \| \leq \epsilon \). Then the Lemma 13 implies that the conditions (F20) are satisfied. This completes the proof. \( \Box \)
c. For block-diagonal input state of a system, a block-diagonal catalyst is enough

Note, for a block-diagonal input state of a system, a block-diagonal catalyst is enough. This can be seen from the fact that the semi-local thermal operations are time-translation symmetric with respect to (sub-)system Hamiltonians and the weighted Hamiltonian of the systems (see Section D2). This is also true in the presence of catalysts. Therefore, the catalytic semi-local thermal operations are time-translation symmetric with respect to the weighted Hamiltonian of the catalyst. Mathematically, for the catalytic semi-local thermal transformation \( \rho_{S_{12}} \otimes \rho_{C_{12}} \rightarrow \Lambda(\rho_{S_{12}} \otimes \rho_{C_{12}}) = \sigma_{S_{12}} \otimes \rho_{C_{12}} \), it means

\[
\Lambda\left( e^{-itH_{S_{12}}} \rho_{S_{12}} \otimes \rho_{C_{12}} e^{itH_{S_{12}}} \right) = e^{-itH_{S_{12}}} \Lambda(\rho_{S_{12}} \otimes \rho_{C_{12}}) e^{itH_{S_{12}}},
\]

(F24)

\[
\Lambda\left( e^{-itH_{S_{12}}} \rho_{S_{12}} \otimes \rho_{C_{12}} e^{itH_{S_{12}}} \right) = e^{-itH_{S_{12}}} \Lambda(\rho_{S_{12}} \otimes \rho_{C_{12}}) e^{itH_{S_{12}}},
\]

(F25)

where \( H_{S_{12}} = \beta \rho \otimes I + I \otimes \rho H_{C_{12}} \) is the weighted Hamiltonian of the catalyst. Due to these time-translation symmetries, the block-diagonal elements of both system \( S_{12} \) and \( C_{12} \) evolve fully independently of the off-diagonal elements. For an initial state \( \rho_{S_{12}} \) block-diagonal in energy bases, the block-diagonal part of the catalyst state only participates during the transformation. Therefore, a catalyst in a state block-diagonal in energy is enough.

d. Avoiding negative \( \alpha \)

The second laws for the transformations between system states, that are block-diagonal in energy, are based on the conditions (F19) for \( \alpha \in [-\infty, \infty] \). However, we can get rid of the negative \( \alpha \) in the conditions by borrowing an ancilla system in a pure state. The only condition is that, after the transformation, we return it with good fidelity. Even a two-qubit system in a pure state is enough to lift all the conditions involving negative \( \alpha \).

**Theorem 17** (Second law for block-diagonal states with fixed Hamiltonian). Consider two states \( \rho_{S_{12}} \) and \( \sigma_{S_{12}} \) that are block-diagonal in the weighted-energy eigenbases, with the associated Hamiltonian \( H_{S_{12}} = H_{S_{12}} \). Additionaly, we are allowed to borrow a two-qubit system \( A_{12} \), with a trivial Hamiltonian, in a pure state \( |0\rangle_1 \otimes |0\rangle_2 \). Then return it with a good fidelity. Then a transformation \( \rho_{S_{12}} \rightarrow \sigma_{S_{12}} \) is possible under semi-local thermal operation if and only if

\[
S_\alpha(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) \geq S_\alpha(\sigma_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}), \quad \forall \alpha \geq 0.
\]

(F26)

**Proof.** Let us first assume that the transformation

\[
\rho_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \rightarrow \sigma_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2
\]

is possible by means of a catalytic semi-local thermal operation. Then, using Theorem 16 and noticing that the Rényi \( \alpha \)-relative entropies \( D_\alpha \) are finite for the state \( |0\rangle_1 \otimes |0\rangle_2 \) only for \( \alpha \geq 0 \), we have

\[
D_\alpha(\rho_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \| \gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{A_1} \otimes \gamma_{A_2}) \geq D_\alpha(\sigma_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \| \gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{A_1} \otimes \gamma_{A_2}), \quad \forall \alpha \geq 0.
\]

(F28)

Moreover, \( D_\alpha(\rho_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \| \gamma_{S_1} \otimes \gamma_{S_2} \otimes \gamma_{A_1} \otimes \gamma_{A_2}) = D_\alpha(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) + D_\alpha(|0\rangle_1 \otimes |0\rangle_2 \| \gamma_{A_1} \otimes \gamma_{A_2}). \) Thus the conditions (F28), in turn, imply the conditions (F26).

Conversely, let us consider that the conditions (F26) (as well as the conditions (F28)) are satisfied. As we have indicated earlier, the \( D_\alpha \)s become infinite with \( |0\rangle_1 \otimes |0\rangle_2 \) for \( \alpha < 0 \). However, we may allow that the final state of the ancillary system \( A_{12} \) is returned in the full-rank state but arbitrarily close to the original state. Then the left-hand side of (F28) remains infinite but the right-hand side becomes finite. Thus, we are led to

\[
D_\alpha(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) \geq D_\alpha(\sigma_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}), \quad \forall \alpha \in \mathbb{R}.
\]

(F29)

Now by Theorem 16, we say that the state \( \rho_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \) can be transformed arbitrarily close to the state \( \sigma_{S_{12}} \otimes |0\rangle_1 \otimes |0\rangle_2 \).

\[ \square \]

3. State transformation with time dependent Hamiltonians

So far we have restricted ourselves to the cases where the system Hamiltonian remains unchanged before and after the transformations. However, in real situations, this restriction is not often respected. To include all these scenarios, we consider the cases where such changes in Hamiltonians are allowed.
Consider a situation where the non-interacting Hamiltonian $H_{S,12} = H_S \otimes I + I \otimes H_S$ of the system $S_{12}$ changes to $H'_{S,12} = H'_S \otimes I + I \otimes H'_S$, along with the state transformation $\rho_{12} \rightarrow \sigma'_{12}$. Here the (’) indicates the state with modified Hamiltonian. Such a change in Hamiltonian often happens due to some time dependencies of the joint Hamiltonian. Then the second laws that incorporate such situations are given in the theorem below.

**Theorem 18** (Second law for block-diagonal states with time-dependent Hamiltonians). **Under a catalytic semi-local thermal operation, a transformation** $(\rho_{S,12}, H_{S,12}) \rightarrow (\sigma'_{S,12}, H'_{S,12})$, **that leads to changes both in system states and the non-interacting system Hamiltonians, is possible if, and only if,**

$$S_\alpha (\rho_{S,12}, \gamma_S \otimes \gamma_S) \geq S_\alpha (\sigma'_{S,12}, \gamma'_S \otimes \gamma'_S), \ \forall \alpha \geq 0, \quad (F30)$$

where $\gamma_S = \frac{e^{-\beta H_S}}{Tr[e^{-\beta H_S}]}$ and $\gamma'_S = \frac{e^{-\beta H'_S}}{Tr[e^{-\beta H'_S}]}$, for $i = 1, 2$.

**Proof.** Note that the total Hamiltonian of the universe is believed to time-independent. Any change happening in the system Hamiltonian can be understood due to a clock system $X$. The joint Hamiltonian of the system and clock system is given by

$$\sum_{t \in T} H(t) \otimes |t\rangle_X, \quad (F31)$$

where $|t\rangle_X$ are some orthonormal basis. Then a change in Hamiltonian $H(t_f) \rightarrow H(t_f)$, along with a transformation in the system state $\rho \rightarrow \sigma$, is equivalent to the change in a joint clock-system state as

$$\rho(t) \otimes |t\rangle_X \rightarrow \sigma(t_f) \otimes |t_f\rangle_X. \quad (F32)$$

We exploit this framework to change the joint non-interacting Hamiltonian of the system, so that

$$H_{S,12} = H_S \otimes I + I \otimes H_S \rightarrow H'_{S,12} = H'_S \otimes I + I \otimes H'_S. \quad (F33)$$

We consider a bipartite clock system $X_{12}$ that is responsible for the change in Hamiltonian of the system $S_{12}$. Since the transition does not depend on the intermediate times, we simply assume the initial state to be $|0\rangle_{X_{12}} = |0\rangle_{X_1} \otimes |0\rangle_{X_2}$, and the final state to be $|1\rangle_{X_{12}} = |1\rangle_{X_1} \otimes |1\rangle_{X_2}$. Therefore, the time-independent joint Hamiltonian of the system and the clock can be written as

$$H_{S_{12},X_{12}} = \left(H_S \otimes |0\rangle_1 \langle 0|_1 + H'_S \otimes |1\rangle_2 \langle 1|_2 \right) \otimes I_{S_1,X_1} + I_{S_2,X_2} \otimes \left(H_S \otimes |0\rangle_1 \langle 0|_1 + H'_S \otimes |1\rangle_2 \langle 1|_2 \right), \quad (F34)$$

$$= H_{S,X_1} \otimes I_{S_2,X_2} + I_{S_1,X_1} \otimes H_{S_2,X_2}. \quad (F35)$$

Here $X_{12}$ plays the role of a switch and it controls the Hamiltonian on the system by choosing its state $|i\rangle_X \otimes |j\rangle_{X_{12}} = |i\rangle_X \otimes |j\rangle_{X_{12}}$. For examples, when the switch $X_{12}$ is in the state $|0\rangle_{00} \otimes |0\rangle_{X_{12}}$, it implements the Hamiltonian $H_{S,12}$ on the system $S_{12}$. On the other hand, when the switch is in the state $|1\rangle_{11} \otimes |1\rangle_{X_{12}}$, it switches the system Hamiltonian to $H'_{S,12}$. Now consider a catalytic semi-local thermal operation that leads to the transformation

$$(\rho_{S_{12}, H_{S_{12}}}) \rightarrow (\sigma'_{S_{12}, H'_{S_{12}}}). \quad (F36)$$

This is equivalent to the transformation between the joint system-switch states block-diagonal in energy, and with the fixed Hamiltonian $H_{S_{12},X_{12}}$,

$$(\rho_{S_{12}, |00\rangle_{X_{12}} \otimes H_{S_{12},X_{12}}) \rightarrow (\sigma'_{S_{12}, |11\rangle_{X_{12}} \otimes H_{S_{12},X_{12}}}) \quad (F37)$$

under a catalytic semi-local thermal operation applied jointly on the system and the clock. Now following the Theorem 17, we cast the necessary and sufficient conditions for the transformation, as

$$S_\alpha (\rho_{S_{12}, |00\rangle_{X_{12}} \otimes \gamma_{S,X_1} \otimes \gamma_{S,X_2}) \geq S_\alpha (\sigma'_{S_{12}, |11\rangle_{X_{12}} \otimes \gamma_{S,X_1} \otimes \gamma_{S,X_2}), \ \forall \alpha \geq 0, \quad (F38)$$

where $\gamma_{S,X_i} = \frac{e^{-\beta H_S}}{Tr[e^{-\beta H_S}]}$, for $i = 1, 2$, are the thermal states correspond to the Hamiltonians $H_{S,X_i}$ and inverse temperatures $\beta_i$. Moreover, we notice that

$$S_\alpha (\rho_{S_{12}, |00\rangle_{X_{12}} \otimes \gamma_{S,X_1} \otimes \gamma_{S,X_2}) \rightarrow S_\alpha (\sigma'_{S_{12}, |11\rangle_{X_{12}} \otimes \gamma_{S,X_1} \otimes \gamma_{S,X_2}), \quad (F39)$$

$$= S_\alpha (\rho_{S_{12}, \gamma_{S_1} \otimes \gamma_{S_2}}) \rightarrow S_\alpha (\sigma'_{S_{12}, \gamma'_{S_1} \otimes \gamma'_{S_2}}).$$

Therefore the necessary and sufficient conditions for the transformation reduce to

$$S_\alpha (\rho_{S_{12}, \gamma_{S_1} \otimes \gamma_{S_2}}) \geq S_\alpha (\sigma'_{S_{12}, \gamma'_{S_1} \otimes \gamma'_{S_2}}), \ \forall \alpha \geq 0. \quad (F40)$$

□
Appendix G: Second laws and transformations between states that are non-block-diagonal in weighted-energy eigenbases

We have already mentioned that the second laws presented above are the necessary and sufficient conditions for the transformation between states that are block-diagonal in the eigenbases of the weighted Hamiltonian \( H_{S_1}^{\beta_1, \beta_2} \). For the states that are not block-diagonal, the second laws only become the necessary conditions. These necessary conditions can be further supplemented by a monotonic measure of the time-translation asymmetry. For a quantum state \( \rho_{S_{12}} \) with the weighted Hamiltonian \( H_{S_{12}}^{\beta_1, \beta_2} \), the asymmetry is defined as

\[
A_\alpha(\rho_{S_{12}}, H_{S_{12}}) = D^\alpha_\beta(\rho_{S_{12}} \parallel D^\beta_\beta(\rho_{S_{12}}))
\]

where the \( D^\beta_\beta(\rho_{S_{12}}) \) is the dephased state in weighted-energy eigenbases, given in Eq. (D20), and the quantum Rényi \( \alpha \)-relative entropy is defined as

\[
D^\alpha_\beta(\rho \parallel \sigma) = \begin{cases} \frac{1}{\alpha-1} \log \text{Tr}(\rho^{1-\alpha} \sigma^\alpha), & \alpha \neq 1, 0 \\ \frac{1}{\alpha-1} \log \text{Tr}(\rho^{1-\alpha} \sigma^\alpha |\sigma^\alpha|), & \alpha > 0. \end{cases}
\]

Note, in the limit \( \alpha \to 1 \), the quantum \( \alpha \)-relative entropy converges to the well known von Neumann relative entropy \( D^1(\rho \parallel \sigma) = \text{Tr}(\rho \log \rho - \rho \log \sigma) \).

Similar to the treatment for state transformation in the presence of single bath [11, 13], we also supplement the necessary condition for state transformation in presence of two baths via cSLTOs, in addition to the second laws for the diagonal states, below.

**Lemma 19.** Consider a transformation \( (\rho_{S_{12}}, H_{S_{12}}) \to (\sigma'_{S_{12}}, H'_{S_{12}}) \) via a cSLTO. Then, the necessary conditions for the transformation are that the measure of asymmetry has to satisfy

\[
A_\alpha(\rho_{S_{12}}, H_{S_{12}}) \geq A_\alpha(\sigma'_{S_{12}}, H'_{S_{12}}), \quad \forall \alpha > 0.
\]

The lemma can be proved in the line of arguments as in [13].

Appendix H: Free-entropy distance

In this section, we establish a formal connection between \( \alpha \)-free-entropies, introduced in the previous section, with thermodynamic work.

A formal connection and equivalence between work and purity have been established in [8, 10]. Here we briefly outline the approach presented in [8]. A thermalization or work extraction process leads an arbitrary system-bath state to a more mixed (or less pure) system-bath state for a subspace with fixed total energy \( E \). These processes are, nothing but randomization (noisy) processes, extensively studied in context purity resource theory [27]. However, there is a subtlety we encounter here, compared to purity resource theory. Nevertheless, one may claim that the thermodynamics is nothing but a purity resource theory constrained by the temperature of the bath and the Hamiltonian of the system [6, 8, 10].

![Figure 6: Work extraction. Say, the sub-systems \( S_1 \) and \( S_2 \) are semi-locally interacting with the baths \( B_1 \) and \( B_2 \) at inverse temperatures \( \beta_1 = 1/T_1 \) and \( \beta_2 = 1/T_2 \), respectively. The work can be extracted by introducing batteries and applying global cSLTOs. See text for more details.](image)

Consider a bipartite system \( S_{12} \), with initial non-interacting Hamiltonian \( H_{S_{12}} = H_{S_1} \otimes I + I \otimes H_{S_2} \), in an initial state \( \rho_{S_{12}} \). After a catalytic semi-local thermal operation, the state and and the Hamiltonian for the system is changed to \( \sigma'_{S_{12}} \) and \( H'_{S_{12}} = H'_{S_1} \otimes I + I \otimes H'_{S_2} \) respectively, i.e.,

\[
(\rho_{S_{12}}, H_{S_{12}}) \to (\sigma'_{S_{12}}, H'_{S_{12}}).
\]

![Figure 6: Work extraction. Say, the sub-systems \( S_1 \) and \( S_2 \) are semi-locally interacting with the baths \( B_1 \) and \( B_2 \) at inverse temperatures \( \beta_1 = 1/T_1 \) and \( \beta_2 = 1/T_2 \), respectively. The work can be extracted by introducing batteries and applying global cSLTOs. See text for more details.](image)
We involve a catalyst $C_{12}$, with the Hamiltonian $H_{C_{12}} = H_C \otimes I + I \otimes H_C$, in a state $\rho_{C_{12}}$ for the transformation.

Our aim is to exploit this transformation to extract free-entropy and thermodynamical work. For that, we also introduce a battery that stores or expends work. We may think that the bipartite battery $W_{12}$ is composed of sub-systems $W_1$ and $W_2$ with the Hamiltonian $H_{W_{12}} = H_W \otimes I + I \otimes H_W$, where the two-level Hamiltonians are $H_W = W_1|W_1\rangle\langle W_1| + H_W = W_2|W_2\rangle\langle W_2|$. The battery sub-system $W_1$ ($W_2$) is locally-interacting with the bath $B_1$ ($B_2$). Note these two battery sub-systems can in principle exchange energy, i.e., work, as this operation is allowed by the catalytic semi-local thermal processes. When the battery sub-systems are thermalized to the temperatures of $B_1$ and $B_2$, the corresponding semi-Gibbs state becomes $\gamma_W \otimes \gamma_W$, where

$$\gamma_W = \frac{1}{1 + e^{-\beta_W W}} \left| 0\rangle\langle 0 | + e^{-\beta_W W | 1\rangle\langle 1 |} \right),$$

with $i = 1, 2$, and $\beta_i$ is the inverse temperature of the bath $B_i$.

Now let us consider the transformation, comprising the system, the catalyst, and the battery,

$$\left(\rho_{S_{12}} \otimes \rho_{C_{12}} \otimes |00\rangle\langle 00 |_{W_{12}}, (H_{S_{12}} \otimes I_{C_{12}} + I_{S_{12}} \otimes H_{C_{12}}) \otimes I_{W_{12}} + I_{S_{12}C_{12}} \otimes H_{W_{12}} \right) \Downarrow \left(\sigma'_{S_{12}} \otimes \rho_{C_{12}} \otimes |W_1 W_2 \rangle W_1 W_2 \rangle \langle W_1 W_2 |_{W_{12}}, (H'_{S_{12}} \otimes I_{C_{12}} + I_{S_{12}} \otimes H_{C_{12}}) \otimes I_{W_{12}} + I_{S_{12}C_{12}} \otimes H_{W_{12}} \right),$$

where we denote $|W_1 W_2 \rangle W_1 W_2 \rangle = |W_1 \rangle W_1 \rangle |W_2 \rangle W_2 \rangle \otimes |W_1 W_2 \rangle W_1 W_2 \rangle$. Then second laws, i.e., Theorem 18, ensure the conditions

$$S_{\alpha}^d(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) \geq S_{\alpha}^d(\sigma'_{S_{12}}, \gamma_{S_1}' \otimes \gamma_{S_2}') \geq S_{\alpha}^d(\sigma_{S_{12}} \otimes \gamma_{S_1} \otimes \gamma_{S_2})-S_{\alpha}^d(\sigma_{S_{12}} \otimes \gamma_{S_1} \otimes \gamma_{S_2}) \geq \beta_1 W_1 + \beta_2 W_2,$$

where $W_1$ ($W_2$) is amount of work stored in the battery sub-system via the transformation in its state $0\rangle0\rangle_{W_1} \rightarrow |W_1 \rangle W_1 \rangle |W_2 \rangle W_2 \rangle$. The bound is true for all $\alpha \geq 0$. Now we derive an important theorem below, based on this observation.

**Theorem 20** (Free-entropy distance). *For a catalytic semi-local thermal operation, leading to a transition $\left(\rho_{S_{12}}, H_{S_{12}} \right) \rightarrow \left(\sigma'_{S_{12}}, H'_{S_{12}} \right)$, the free-entropy distance between the initial and final states is given by

$$S_{d}(\rho_{12} \rightarrow \sigma'_{12}) = \inf_{\alpha \geq 0} \left[S_{\alpha}^d(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) - S_{\alpha}^d(\sigma'_{S_{12}}, \gamma_{S_1}' \otimes \gamma_{S_2}') \right],$$

and

$$= \beta_1 W_1 + \beta_2 W_2.$$*

Theorem 20 leads to several interesting results. Now in terms of the free-entropy distance, we can quantify these quantities, as in the following.

**Corollary 21** (Extractable free-entropy and free-entropy cost). *For a transformation between the block-diagonal states, $\left(\rho_{S_{12}}, H_{S_{12}} \right) \rightarrow \left(\sigma'_{S_{12}}, H'_{S_{12}} \right)$, under catalytic semi-local thermal operations, the extractable free-entropy $S_{\text{ext}}^d$ and the free-entropy cost $S_{\text{cost}}^d$ for the reverse process, are given by

$$S_{\text{ext}}^d(\rho_{12} \rightarrow \sigma'_{12}) = \sup_{\alpha \geq 0} \left[S_{\alpha}^d(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) - S_{\alpha}^d(\sigma_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) \right] = S_{d}(\rho_{12} \rightarrow \sigma'_{12}),$$

and

$$S_{\text{cost}}^d(\sigma'_{12} \rightarrow \rho_{12}) = -\inf_{\alpha \geq 0} \left[S_{\alpha}^d(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) - S_{\alpha}^d(\sigma_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) \right].$$

It is clear that the free-entropy that we can extract from the process is in general lower than the free-entropy to be expended to reverse the process. To see this, let us consider the transformation (H1) and assume $S_{\text{ext}}^d(\rho_{S_{12}} \rightarrow \sigma'_{S_{12}}) > 0$. Then,

$$S_{\text{ext}}^d(\rho_{S_{12}} \rightarrow \sigma'_{S_{12}}) \leq -S_{\text{cost}}^d(\sigma'_{S_{12}} \rightarrow \rho_{S_{12}}).$$

Therefore, thermodinamics in this regime is fundamentally irreversible, analogous to the cases with single bath [8]. With the help of free-entropy distance, we are also able to compute the distillable free-entropy and free-entropy of formation for a state.

**Corollary 22** (Distillable free-entropy and free-entropy of formation). *In the situation where the $\sigma_{S_{12}} = \gamma_{S_1} \otimes \gamma_{S_2}$, and the system Hamiltonian does not change, the Corollary 21 leads us to quantify distillable free-entropy $S_{\text{dist}}^d$ for the process $\rho_{S_{12}} \rightarrow \gamma_{S_1} \otimes \gamma_{S_2}$, and the free-entropy of formation $S_{\text{form}}^d$ for the process $\gamma_{S_1} \otimes \gamma_{S_2} \rightarrow \rho_{S_{12}}$, as

$$S_{\text{dist}}^d(\rho_{S_{12}}) = D_0(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) = -\log \text{Tr} (\Pi_{\rho_{S_{12}}} \gamma_{S_1} \otimes \gamma_{S_2}),$$

and

$$S_{\text{form}}^d(\rho_{S_{12}}) = D_{\infty}(\rho_{S_{12}} \| \gamma_{S_1} \otimes \gamma_{S_2}) = \log \min \{|A : \rho_{S_{12}} \leq A(\gamma_{S_1} \otimes \gamma_{S_2})\}. $$
Till now we have illustrated the second laws for transformation among the states block-diagonal in weighted-energy eigenbases. Now it would be interesting to study the processes occur in a heat engine and generalize the laws. This is what we are going to do in the next section.

Appendix I: Second laws: quantum heat engines

The heat engines are those that convert heat into work. In general, an engine works in a cycle between two baths with different temperatures. As we see below, the framework developed based on catalytic semi-local thermal operations can be easily used to characterize the heat engines. In fact, the process in a heat engine becomes a special case of the general transformation we have studied above.

Figure 7. Engine operating in a one-step cycle using a bipartite system \( S_{12} \) and semi-local thermal operations. The sub-system \( S_1 \) with the Hamiltonian \( H_{S_1} \) semi-locally interacts with the bath \( B_1 \) at inverse temperature \( \beta_1 = 1/T_1 \). Similarly, the sub-system \( S_2 \) with the Hamiltonian \( H_{S_2} \) semi-locally interacts with the bath \( B_2 \) at inverse temperature \( \beta_2 = 1/T_2 \). Using cSLTOs, it executes the transformation shown in Proposition 23. In the next cycle, the step repeats just by letting \( S_1 \) and \( S_2 \) to semi-locally interacting with the baths \( B_2 \) and \( B_1 \) respectively.

Traditionally, a heat engine (or a refrigerator) is composed of several components and operates in several steps. For example, a typical Carnot engine is made up of two baths with non-identical temperatures, working-systems (say ideal gas) and a piston that carries the extracted work out of the engine. It operates in cycle, comprising four steps; (a) the working-system \( S \), with Hamiltonian \( H_S \), interacts with a bath say \( B_1 \) and thermalize to its inverse temperature \( \beta_1 \), (b) then an adiabatic process changes the Hamiltonian of the working-system to \( H_S' \), (c) the modified working-system is then brought in touch with the other bath \( B_2 \) and let it thermalize to the corresponding inverse temperature \( \beta_2 \), and finally, (d) the Hamiltonian of the working-system is adiabatically changed to the initial Hamiltonian \( H_S \) to complete the cycle. As we show below, in our framework, we can perform all these four steps in one stroke!

1. Transformations in quantum and nano-scale heat engines

The heat engines (or refrigerators) proposed here are composed three major components, as mentioned below.

1. Two considerably large heat baths \( B_1 \) and \( B_2 \), with inverse temperatures \( \beta_1 = 1/T_1 \) and \( \beta_2 = 1/T_2 \) respectively, and \( \beta_1 < \beta_2 \).

2. A bipartite working-system \( S_{12} \) composed of two sub-systems \( S_1 \) and \( S_2 \) with non-interacting Hamiltonian \( H_{S_{12}} = H_{S_1} \otimes I + I \otimes H_{S_2} \). We may need a catalyst additionally, but we can safely incorporate it as part of the working-system.

3. A bipartite battery \( W_{12} \) that stores or supplies work. We assume that the battery \( W_{12} \) is composed of two sub-systems \( W_1 \) and \( W_2 \) with corresponding local Hamiltonians \( H_{W_1} = W_1[W_1]W_1 \) and \( H_{W_2} = W_2[W_2]W_2 \), so that the non-interacting joint Hamiltonian becomes \( H_{W_{12}} = H_{W_1} \otimes I + I \otimes H_{W_2} \). Without loss of generality, we have further assume that the battery sub-systems are two-level systems. The energy of the battery can both be positive and negative. These two sub-systems of the battery can in principle exchange energy (i.e., work) among themselves, as this is allowed by the semi-local thermal processes, but always remain in pure energy eigenstates of their corresponding Hamiltonians.

Let us propose the one-step cycle of a heat engine below.

**Proposition 23** (Operation cycle in a heat engine). Consider the initial joint state and the Hamiltonian of the of the system-battery composite are \( \rho_{S_{12}} \otimes |0\rangle\langle 0|_{W_{12}} \) and \( H_{S_{12},W_{12}} = H_{S_1} \otimes I_{S_2W_{12}} + I_{S_1} \otimes H_{S_2} \otimes I_{W_{12}} + I_{S_{12}} \otimes H_{W_{12}} \) respectively. The composites \( S_1W_1 \) and \( S_2W_2 \) are semi-locally interacting with the baths \( B_1 \) and \( B_1 \), where the baths are at inverse temperatures \( \beta_1 \) and \( \beta_2 \) respectively, and \( \beta_1 < \beta_2 \). Then, the engine operates in a cycle by implementing the step

\[
(\rho_{S_{12}} \otimes |0\rangle\langle 0|_{W_{12}}, \ H_{S_{12},W_{12}}) \longrightarrow (\sigma'_{S_{12}} \otimes |W\rangle\langle W|_{W_{12}}, \ H'_{S_{12},W_{12}}),
\]

with the modified Hamiltonian \( H'_{S_{12},W_{12}} = H'_{S_1} \otimes I_{S_2W_{12}} + I_{S_1} \otimes H'_{S_2} \otimes I_{W_{12}} + I_{S_{12}} \otimes H_{W_{12}} \), so that it satisfies the conditions

\[
\sigma'_{S_{12}} = U_{S_1 \leftrightarrow S_2}^{SWAP} (\rho_{S_{12}}), \quad H'_{S_1} = H_{S_2}, \quad \text{and} \quad H'_{S_2} = H_{S_1},
\]

where the unitary \( U_{S_1 \leftrightarrow S_2}^{SWAP} \) performs a SWAP operation between sub-systems \( S_1 \) and \( S_2 \).
The next cycle starts by inter-changing the interactions between sub-systems and baths. In other words, the first engine cycle starts with the (semi-local) interactions as $B_1S_1W_1 - W_2S_2B_2$ and then, in the next cycle, engine interchanges the interactions as $B_1S_2W_1 - W_2S_1B_2$, and continues. See Fig. 7 for a schematic for such operation.

If we analyze the transformation more carefully, we shall realize that there are two sub-processes taking place simultaneously. These are (i) the sub-transformation from $\rho_{S_2} = \text{Tr}_S[\rho_{S_2}], \gamma_{S_2} \to \rho_{S_1} = \text{Tr}_S[\rho_{S_1}]$, by exploiting the semi-local interaction with the bath $B_1$, and (ii) the reverse sub-transformation $\rho_{S_2} \to \rho_{S_1}$ by using the semi-local interaction with the bath $B_2$, while swapping $(S_1 \leftrightarrow S_2)$ global state of the system. Therefore, from the view of sub-system transformation, there are two sub-processes occurring at the same time which are exactly opposite to each other while keeping the correlations intact, and these are taking place in interactions with two different baths.

2. Second laws for heat engines and statements of second laws in the one-shot finite-size regime

The transformations happening in every cycle of engine operation are restricted ones, compared to the general cases consider before, as the initial and final system states and the Hamiltonians of the subsystems are constrained to ensure repeatability of the engine operations. Therefore, using Theorem 18, we may propose the conditions for the feasibility of a heat engine that operates spontaneously.

**Theorem 24** (Second laws for heat engines). An engine operating using the cycle proposed in Proposition 23, can operate spontaneously if, and only if,

$$S_\alpha (\rho_{S_12}, \gamma_{S_1} \otimes \gamma_{S_2}) \geq S_\alpha (\sigma_{S_12}', \gamma_{S_1} \otimes \gamma_{S_2}'), \quad \forall \alpha \geq 0,$$

where $\gamma_{S_i} = \frac{\exp(H_{S_i})}{\text{Tr}[\exp(H_{S_i})]}$, for $i = 1, 2$, and $\gamma_{S_i} = \frac{\exp(H_{S_i})}{\text{Tr}[\exp(H_{S_i})]}$ and $\gamma_{S_i}' = \frac{\exp(H_{S_i}')}{\text{Tr}[\exp(H_{S_i}')]}$.

This indicates that given an initial system state and non-interacting system Hamiltonian, the engineer has to decide first which sub-system to attach with which bath. With the choice for which the above conditions are satisfied, the engine can operate spontaneously. As it will be discussed in Section 13, this imposes an asymmetry in the preferred transformation and thereby choosing a cycle that does not require an external free-entropy (or work) supply. This asymmetry, as the consequence of Theorem 24, is, in fact, the essence of Clausius, Kelvin-Plank, and Carnot statements of the second law. Now, using the Theorem 20, we can also quantify the free-entropy distance in every cycle of engine operation, as given below.

**Theorem 25** (Free-entropy distance for a cycle in heat engine). For an engine, that is undergoing the cycle proposed in Proposition 23, the free-entropy distance between the states before and after the cycle is given by

$$S^f_{\alpha} (\rho_{S_12} \rightarrow \sigma'_{S_12}) = \inf \left\{ S_\alpha (\rho_{S_12}, \gamma_{S_1} \otimes \gamma_{S_2}) - S_\alpha (\sigma_{S_12}', \gamma_{S_1} \otimes \gamma_{S_2}'), \quad \forall \alpha \geq 0 \right\},$$

and the amount of guaranteed work one can extract from an engine, and the minimum work to be expended to run a refrigerator.

**Corollary 26** (Extractable work per engine cycle). An engine working in a cycle, following the step as in Proposition 23, a non-zero work can be extracted in each cycle if, and only if,

$$S^\text{eng} (\rho_{S_12} \rightarrow \sigma'_{S_12}) = \inf \left\{ S^\text{eng} (\rho_{S_12} \rightarrow \sigma'_{S_12}) \right\} = \beta_1 W_1^e + \beta_2 W_2^e \geq 0,$$

and the amount of guaranteed extractable work is given by

$$W^\text{eng}_{\text{ext}} = W_1^e + W_2^e.$$
Corollary 27. For an engine working in a cycle following the step as in Proposition 23, various statements of one-shot second laws are given below.

Clausius statement: The work extracted in the presence of the hot bath is larger than the work expended in the presence of the cold bath, i.e.,
\[ W_1^e > W_2^e. \] (19)

Kelvin-Planck statement: The net extractable work in each cycle is strictly lower than the work extracted in the sub-process occurs in the presence of the hot bath, i.e.,
\[ W_{ext}^e = W_1^e + W_2^e < W_1^e. \] (110)

Carnot statement: The one-shot efficiencies of work extraction in each cycle is given by
\[ \eta_1^{eng} = \frac{W_{ext}^e}{W_1^e} \geq 1 - \frac{\beta_1}{\beta_2}, \quad \eta_2^{eng} = \frac{W_{ext}^e}{W_2^e} \leq \frac{\beta_2}{\beta_1} - 1. \] (111)

Let us consider the reverse process that occurs in a refrigerator.

Corollary 28 (Work cost per refrigeration cycle). An engine working in a cycle, following the step as in Proposition 23, can operate as a refrigerator if, and only if, the minimum amount of free-entropy supplied is
\[ S_{ref}^{eng} (\rho_{S_{12}}' \rightarrow \rho_{S_{12}}) = - \sup_{\alpha \geq 0} S_a^{eng} (\rho_{S_{12}}' \rightarrow \rho_{S_{12}}') = \beta_1 W_1^r + \beta_2 W_2^r \leq 0, \] (112)
and then the minimum amount of work required to perform the refrigeration cycle is given by
\[ W_{cost}^{ref} = |W_1^r| - W_2^r. \] (113)

Since refrigeration is exactly the reverse to the process of work extraction in a heat engine, the sub-process happening in interaction with the hotter bath requires more work than the work produced in the sub-process to reverse the transformation in interacting with the colder bath. For this reason, \( W_1^r \) is negative and \( W_2^r \), and further \( |W_1^r| > W_2^r \) as \( \beta_1 < \beta_2 \). Thus the minimum amount of work needed to run the refrigeration cycle is \( W_{cost}^{ref} = |W_1^r| - W_2^r \).

3. Many Clausius, Kelvin-Planck and Carnot statements of many second laws

Various statements of the second law in classical thermodynamics, in fact, impose certain restrictions on heat flow from one bath to another bath. We can reformulate these second law statements using the formulation presented above. Since, in classical heat engine the working system goes through transformations with one bath at a time, we can safely assume a cycle composed of four steps: (a) transformation \( (\rho, H_S) \rightarrow (\sigma, H_S) \) in presence of bath \( B_1 \) and inverse temperature \( \beta_1 \), (b) transformation \( (\sigma, H_S) \rightarrow (\sigma', H_S') \) without any interaction with a bath, (c) transformation \( (\sigma, H_S') \rightarrow (\rho, H_S') \) in interaction with the bath \( B_2 \) at inverse temperature \( \beta_2 \), and the final step (d) transformation \( (\rho, H_S') \rightarrow (\rho, H_S) \) without any interaction with a bath. Note that, while the steps (a) and (c) are isothermal transformations, the steps (b) and (d) are adiabatic transformations.

All these transformations, comprising four different steps, can be performed in one step in our framework. That is nothing but performing the operation cycle proposed in Proposition 23, except we assume the initially uncorrelated state, i.e.,
\[ \rho_{S_{12}} = \rho \otimes \sigma, \] (114)
and the transformation in the cycle becomes
\[ (\rho \otimes \sigma, H_{S_1} \otimes I + I \otimes H_{S_1}) \rightarrow (\sigma \otimes \rho, H_{S_1} \otimes I + I \otimes H_{S_1}), \] (115)
where \( H_{S_1} = H_S \) and \( H_{S_2} = H_S' \). For such a transformation, we may rewrite the second laws as in the following.

Theorem 29. An engine operating using the cycle proposed above can operate spontaneously under semi-local thermal operations if, and only if,
\[ \beta_1 W_1^{(a)} + \beta_2 W_2^{(a)} \geq 0, \quad \forall a > 0 \] (116)
\[ \beta_1 W_1^{\alpha} = S_a (\rho, \gamma_{s_1}) - S_a (\sigma, \gamma'_{s_1}), \] 
\[ \beta_2 W_2^{\alpha} = S_a (\sigma, \gamma_{s_1}) - S_a (\rho, \gamma'_{s_2}), \]  
\[ \gamma'_{s_1} = \frac{e^{\beta_1 \mu_{s_1}}}{\text{Tr}[e^{\beta_1 \mu_{s_1}}]} \quad \text{and} \quad \gamma'_{s_2} = \frac{e^{\beta_2 \mu_{s_2}}}{\text{Tr}[e^{\beta_2 \mu_{s_2}}]} . \]  

Proof. We note that, from Theorem 24, an engine can operate spontaneously if, and only if,

\[ S_a (\rho \otimes \sigma, \gamma_{s_1} \otimes \gamma_{s_2}) \geq S_a (\sigma \otimes \rho, \gamma'_{s_1} \otimes \gamma'_{s_2}), \quad \forall \alpha \geq 0. \]  

With simple manipulations and the notations of local \( \alpha \)-free-entropies (similar to the work distance studied in [10]), we can immediately recover the Theorem 29.

Now, we shall introduce and generalize the statements of the Clausius, Kelvin-Planck and Carnot statements of second laws in terms of the \( \alpha \)-works \( W_{1/2}^{\alpha} \) below. All these generalized statements can be seen as the simple corollaries of the Theorem 29.

**Corollary 30** (Clausius \( \alpha \)-statements of second laws). An engine, working in a cycle using the step Eq. (115) can operate spontaneously for \( \beta_1 < \beta_2 \) if, and only if,

\[ W_1^{\alpha} + W_2^{\alpha} > 0, \quad \forall \alpha \geq 0. \]  

Therefore, the amount of \( \alpha \)-work that is drawn from the transition \( \rho \rightarrow \sigma \) in the presence hot bath (\( B_1 \)) is larger than the expended work to reverse transformation in presence of the cold bath (\( B_2 \)). It clearly indicates that the flow of energy has to be from the hot to the cold baths. This is exactly the many Clausius \( \alpha \)-statements that to be satisfied in this quantum regime.

**Corollary 31** (Kelvin-Planck \( \alpha \)-statements of second law). For an engine, working in a cycle using the step Eq. (115) with \( \beta_1 < \beta_2 \) and operates spontaneously, the \( \alpha \)-works satisfy

\[ W_{\text{ext}}^{\alpha} = W_1^{\alpha} + W_2^{\alpha} < W_1^{\alpha}, \quad \forall \alpha \geq 0. \]  

Note the \( W_{\text{ext}}^{\alpha} \) is exactly the extractable \( \alpha \)-work in each cycle. Thus, the Kelvin-Planck statement is generalized to the one-shot limit. A simple manipulation recovers the equivalent Carnot statements too.

**Corollary 32** (Carnot \( \alpha \)-statements of second laws). For an engine, operating spontaneously in a cycle using the step Eq. (115) with \( \beta_1 < \beta_2 \), the efficiencies of \( \alpha \)-work extraction \( \eta_1^{\alpha} \) and \( \eta_2^{\alpha} \) satisfy

\[ \eta_1^{\alpha} = 1 - \beta_1 \frac{W_1^{\alpha}}{W_1^{\alpha}} \geq 1 - \beta_1 \frac{W_1^{\alpha}}{W_1^{\alpha}} \leq \beta_2 \frac{W_1^{\alpha}}{W_1^{\alpha}} - 1, \quad \forall \alpha \geq 0. \]  

Appendix J: Asymptotic equipartition

It is known that all the Rényi \( \alpha \)-entropies and \( \alpha \)-relative entropies converge to von Neuman entropy and relative entropy in the asymptotic limit (or i.i.d. limit), i.e.,

\[ \lim_{N \rightarrow \infty} \frac{1}{N} H_\alpha (\rho^N) = H_1 (\rho) = -\text{Tr} \rho \log \rho, \quad \forall \alpha, \]  
\[ \lim_{N \rightarrow \infty} \frac{1}{N} D_\alpha (\rho^N \| \sigma^N) = D_1 (\rho \| \sigma) = \text{Tr} (\rho \log \rho - \rho \log \sigma), \quad \forall \alpha. \]  

Similarly, all the \( \alpha \)-free-entropies reduce to the Helmholtz free-entropy, as

\[ \lim_{N \rightarrow \infty} \frac{1}{N} S_\alpha (\rho^N_{s_{12}}, (\gamma_{s_1} \otimes \gamma_{s_2})^N_{s_{12}}) = S_1 (\rho_{s_{12}}, \gamma_{s_1} \otimes \gamma_{s_2}), \quad \forall \alpha. \]  

Therefore, in the asymptotic limit, there is only one free-entropy and that is the Helmholtz free-entropy. The many second laws in the one-shot finite-size regime converge to one second law in the asymptotic regime. Consider a transformation in the asymptotic regime via a cSLTO, where the individual system transformations as

\[ (\rho_{s_{12}}, H_{s_{12}}) \rightarrow (\sigma'_{s_{12}}, H'_{s_{12}}). \]
The amount of extractable free-entropy or the free-entropy distance per copy of the system, given the initial and the final states, is
\[ S_d(\rho_{S_{12}} \rightarrow \sigma'_{S_{12}}) = S_1(\rho_{S_{12}}, \gamma_{S_1} \otimes \gamma_{S_2}) - S_1(\sigma'_{S_{12}}, \gamma'_{S_1} \otimes \gamma'_{S_2}). \] (J5)

Note, for the reverse transformation \((\sigma'_{S_{12}}, H'_{S_{12}}) \rightarrow (\rho_{S_{12}}, H_{S_{12}})\), the free-entropy cost per copy of the system is
\[ S_d(\sigma'_{S_{12}} \rightarrow \rho_{S_{12}}) = -S_d(\rho_{S_{12}} \rightarrow \sigma'_{S_{12}}), \] (J6)

which is exactly equal and opposite to extractable free-entropy. As a consequence, the thermodynamic reversibility is recovered in the asymptotic regime.

We recall that there is a free-entropy locking in the quantum states that have quantum correlations in the one-shot finite-size regime. The cSLTOs are time translation symmetric with respect to the weighted Hamiltonian \(H_{S_{12}}^{\beta_1 \beta_2}\) (see Appendix D 2). A quantum state \(\rho_{S_{12}}\) that has superposition in the eigenbases of \(H_{S_{12}}^{\beta_1 \beta_2}\) cannot be rotated to a block-diagonal form by using a cSLTO. Further, the off-diagonal elements of \(\rho_{S_{12}}\) evolve independently of the block-diagonal elements under cSLTOs, and the cSLTOs can only access the block-diagonal elements. However, in the asymptotic limit, where \(N \rightarrow \infty\), all states become symmetric with respect to the weighted Hamiltonian on average, and this is because of the fact that
\[
\lim_{N \rightarrow \infty} \frac{1}{N} \left| \rho_{S_{12}}^{\otimes N} \sum_{x=0}^{N-1} \mathbb{I}^{\otimes x} \otimes H_{S_{12}}^{\beta_1 \beta_2} \otimes \mathbb{I}^{\otimes (N-x-1)} \right| = 0, \forall \rho_{S_{12}}. \] (J7)

So, an arbitrary state can be written in the block-diagonal form of the weighted Hamiltonian in the asymptotic regime on average. It means that a state which is non-block-diagonal in one-shot finite-size regime becomes block-diagonal (on average) in the weighted-energy eigenbases in the asymptotic regime. Consequently, the locked free-entropy due to the presence of quantum superpositions and correlations in a state can be accessed and extracted in the asymptotic regime.