# Zero-fluctuation quantum work extraction

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(Received 15 March 2024; accepted 7 June 2024; published 12 July 2024)

We study the possibility of deterministic protocols for extracting work from quantum systems. Focusing on the two-point measurement work extraction scenario, we prove that, with enough copies of the system, such zero-fluctuation protocols always exist if the Hamiltonian has a rational spectrum. Leveraging this result, we show that for any Hamiltonian, it is possible to construct a unitary driving protocol on sufficiently many copies of the system with work fluctuations strictly bounded within an arbitrary interval $\pm\delta$, albeit requiring exponentially many copies in $1/\delta$.

DOI: 10.1103/PhysRevA.110.012213

## I. INTRODUCTION

The definition of thermodynamic work in quantum systems has been a longstanding question [1–7]: at microscopic scales, the work that can be extracted from a system acquires a stochastic nature, due to thermal [8,9] and quantum fluctuations [10–13]. A prominent paradigm for defining quantum work is the two-point measurement (TPM) scheme [14–17], which provides a conceptually simple operational paradigm for defining fluctuating work in the quantum regime and forms the basis for various quantum fluctuation theorems [18–21]. The TPM protocol operates as follows: first, a projective energy measurement is performed on the system, collapsing its state into an energy eigenstate $|\epsilon_i\rangle$. Next, the system evolves unitarily under the action of an external agent. Finally, a second energy measurement reveals the final energy state $|\epsilon_j\rangle$ after evolution. By comparing the initial and final energies $\epsilon_i$ and $\epsilon_j$, one can define the stochastic work performed on the system as $w = \epsilon_i - \epsilon_j$. Repeating this TPM procedure many times generates a work probability distribution $\mathrm{P}(w)$.

A key optimization goal is to extract the maximum process average work $\langle W\rangle$ by suitably choosing the driving unitary $\hat{U}$. A fundamental bounds on $\langle W\rangle$ is provided by the *ergotropy* [22,23]—the energy difference between the initial state of the quantum system and its corresponding *passive state* [24,25]. More sophisticated protocols have been conceived in literature and employ nonlocal operations to suppress the fluctuations of the extracted work $w$ around its average value $\langle W\rangle$ [26–30]. In particular, Ref. [31] showed that by collectively processing $n$ copies of a quantum system, the probability $\mathrm{P}(|w - \langle W\rangle| > \delta)$ of getting work fluctuations larger than a threshold $\delta > 0$ can be made to decay exponentially in $n$. The concept of "$\epsilon$-deterministic" work extraction has also been proposed, to indicate protocols that completely suppress fluctuations, except for a small failure probability [11,32]. Other studies investigated the maximization of risk-averse utility functions of the work probability distribution [33,34].

Our work goes beyond [31] to construct explicit protocols where the work fluctuations can be completely eliminated, such that the extracted work takes a single deterministic value $W^{(\mathrm{det})}$. In other word, we find unitary evolution transformations with the property that the final energy of the system at the end of the TPM process is completely determined by the result of the first measurement, and the second measurement is inconsequential. We prove that such protocols always exist for systems with rational spectra: if we collectively process multiple copies, then a finite $W^{(\mathrm{det})} > 0$ can be extracted with zero fluctuations. For irrational spectra, for which a deterministic work extraction protocol may not be possible, we prove that with a sufficiently large number of copies we can always find a TPM work extraction protocol whose fluctuations can be strictly bound by an arbitrarily small constant [i.e., such that $\mathrm{P}(|w - \langle W\rangle| > \delta) = 0$]. By using the TPM framework for defining the work extracted from a system, we are assuming that it is possible to perform operationally ideal projective measurements of the energy of the system. Although, in practice, every measurement carries an energy cost (and a perfectly ideal projective measurement would carry an infinite energy cost [35], from the third law of thermodynamics), in this work we assume that the energetic cost to perform a sufficiently precise measurement is negligible compared with the energy scale of the quantum system.

Compared with the results of Ref. [31], our zero-fluctuation protocols apply to a narrower regime of parameter space, but provide the strongest possible guarantee on work fluctuations by eliminating them completely. We identify permutations of energy levels between multiple copies that enable zero-fluctuation work extraction. For general spectra, we provide a stronger constraints on fluctuations than Ref. [31]—ensuring that the extracted work $w$ from its expected value can be strictly bounded in a narrow band. The concept of work extraction with bounded fluctuations was first introduced in Ref. [36], in which the authors show the existence of thermodynamic cycles with bounded fluctuation in some qubit

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and qutrit quantum systems; in this work, we generalize their results by providing a way to construct a bounded-fluctuations work extraction protocol for any system Hamiltonian $\hat{H}$. Our zero-fluctuation protocols could find applications in quantum heat engines or batteries, where reliable work output is critical. The concept may also extend to bounding fluctuations of other quantities through global quantum operations, and help to introduce designs for stable quantum devices functioning in the finite copy regime.

The rest of paper is organized as follows: In Sec. II we define the notation. In Sec. III we review the structure of TPM measurements and formally introduce the problem of finding the maximum amount of work $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H})$ that can be extracted deterministically from a quantum system described by a Hamiltonian $\hat{H}$ initialized in the state $\hat{\rho}$. In Sec. IV we present some basic properties of the functional $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H})$, showing that it only depends on the spectrum of the Hamiltonian, and on the occupancy levels of the input state $\hat{\rho}$. In Sec. V we show that $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H})$ is superadditive in the number $n$ of copies of the system and define the *asymptotic maximum deterministic work-extraction rate* $\mathcal{R}(\mathcal{A},\hat{H})$, which quantifies how much can be deterministically retrieved from a large $n\to\infty$ number of copies of the system. In Sec. V, some upper bounds for $\mathcal{R}(\mathcal{A},\hat{H})$ are presented. Section VI is devoted to the presentation of same simple examples which are useful to shed light on the problem. In Sec. VII, we show that if the eigenvalues of the system Hamiltonian $\hat{H}$ are commensurable, then it is always possible to extract deterministically a nonzero amount of work for a sufficiently large number of copies of the system [i.e., $\mathcal{R}(\mathcal{A},\hat{H})>0$]. Our proof is constructive, meaning that we provide an explicit protocol for deterministic work extraction for any Hamiltonian $\hat{H}$ with a commensurable spectrum.

Building upon this result, in Sec. VIII we show that, by approximating a generic Hamiltonian $\hat{H}$ to a $\delta$-close Hamiltonian $\hat{H}'$ with commensurable eigenvalues, we can construct (for a sufficiently large number of copies) a work extraction protocol whose fluctuations can be strictly bounded by an arbitrarily small constant $2\delta$. In Sec. IX we provide another estimation of the asymptotic rate $\mathcal{R}(\mathcal{A},\hat{H})$ using the local asymptotic normality of the distribution of energy eigenstates. This is not an upper bound neither a lower bound, but we heuristically expect it to be "close" to the actual value of $\mathcal{R}(\mathcal{A},\hat{H})$ in most cases. Conclusions are drawn in Sec. X. The paper also contains a couple of technical Appendixes.

## II. NOTATION

Consider a quantum system described by a $d$-dimensional Hilbert space $\mathcal{H}$, whose Hamiltonian

$$\hat{H}:=\sum_{i=0}^{M-1}\epsilon_i\hat{\Pi}_i \tag{1}$$

is characterized by $M$ ($\leqslant d$) distinct eigenvalues $\{\epsilon_0,\epsilon_1,\dots,\epsilon_{M-1}\}$ of degeneracies $\{d_0,d_1,\dots,d_{M-1}\}$, $\sum_{i=1}^{M-1}d_i=d$. In the above expression the operators $\hat{\Pi}_0,\hat{\Pi}_1,\dots,\hat{\Pi}_{M-1}$ form a complete set of orthonormal projectors ($\sum_{i=0}^{M-1}\hat{\Pi}_i=\hat{\mathbb{1}}$, $\hat{\Pi}_i\hat{\Pi}_{i'}=\delta_{i,i'}\hat{\Pi}_i$) associated with the energy eigenspaces $\mathcal{H}_0,\mathcal{H}_1,\dots,\mathcal{H}_{M-1}$ of $\hat{H}$ ($\mathcal{H}=\oplus_{i=0}^{M-1}\mathcal{H}_i$, $\dim\mathcal{H}_i=d_i$). Without loss of generality we set equal to zero the ground energy of the model and assume the following ordering for the spectral elements of $\hat{H}$:

$$\epsilon_0=0,$$
$$\epsilon_j<\epsilon_{j+1}\ \forall\ j\in\{0,\dots,M-2\}.$$

We also define the linear, completely positive trace preserving (LCPTP) channel

$$\Phi(\cdots):=\sum_{i=0}^{M-1}\hat{\Pi}_i\cdots\hat{\Pi}_i, \tag{2}$$

which induces full decoherence with respect to the energy eigenspaces of the system.

Given hence $\hat{\rho}$ an arbitrary quantum state of the system, we define

$$P(i|\hat{\rho}):=\mathrm{Tr}[\hat{\Pi}_i\hat{\rho}], \tag{3}$$

as the population it assigns to the $i$th energy eigenspace $\mathcal{H}_i$ and call *nonzero energy level set* $\mathbb{S}[\hat{\rho}]$ the set of energy levels which have a nonzero population, i.e.,

$$\mathbb{S}[\hat{\rho}]:=\{i:P(i|\hat{\rho})>0\}. \tag{4}$$

The energy diagonal counterpart of $\hat{\rho}$ obtained by the application of the transformation $\Phi$, can be expressed as

$$\Phi(\hat{\rho}):=\sum_{i\in\mathbb{S}[\hat{\rho}]}\hat{\Pi}_i\hat{\rho}\hat{\Pi}_i=\sum_{i\in\mathbb{S}[\hat{\rho}]}P(i|\hat{\rho})\hat{\rho}_i, \tag{5}$$

where for $i\in\mathbb{S}[\hat{\rho}]$,

$$\hat{\rho}_i:=\hat{\Pi}_i\hat{\rho}\hat{\Pi}_i/P(i|\hat{\rho})=\sum_{k=0}^{r_i-1}p_{i,k}|\epsilon_{i,k}\rangle\langle\epsilon_{i,k}| \tag{6}$$

is the projected component of $\hat{\rho}$ on $\mathcal{H}_i$. In this expression $r_i$ represents the rank of the matrix $\hat{\rho}_i$, $p_{i,k}>0$ its nonzero eigenvalues, and $|\epsilon_{i,k}\rangle\in\mathcal{H}_i$ the corresponding eigenvector. Notice that by construction one has

$$P(i|\hat{\rho})=P(i|\Phi(\hat{\rho})),\quad \mathbb{S}[\hat{\rho}]=\mathbb{S}[\Phi(\hat{\rho})], \tag{7}$$

and that the support space of $\Phi(\hat{\rho})$

$$\mathrm{Supp}[\Phi(\hat{\rho})]:=\{|\psi\rangle:\Phi(\hat{\rho})|\psi\rangle\neq 0\}, \tag{8}$$

is a proper subset of the direct sum of the energy eigenspaces of the model over the elements of $\mathbb{S}[\hat{\rho}]$. More precisely we can write

$$\mathrm{Supp}[\Phi(\hat{\rho})]=\bigoplus_{i\in\mathbb{S}[\hat{\rho}]}\mathcal{H}_i[\Phi(\hat{\rho})], \tag{9}$$

where for $i\in\mathbb{S}[\hat{\rho}]$,

$$\mathcal{H}_i[\Phi(\hat{\rho})]:=\mathrm{Span}\{|\epsilon_{i,k}\rangle;k=1,\dots,r_i\}\subseteq\mathcal{H}_i, \tag{10}$$

represents the $r_i$-dimensional subset of $\mathcal{H}_i$ where $\Phi(\hat{\rho})$ has no zero population [see Eq. (6)]. In case $\hat{H}$ is not degenerate (i.e., when $M=d$) then the inclusion in the last (9) can be replaced by an identity implying that $\mathrm{Supp}[\Phi(\hat{\rho})]$ is fully characterized by the nonempty population index subset of $\hat{\rho}$. For degenerate Hamiltonians such correspondence breaks since, while it still true that states $\hat{\rho}$ and $\hat{\varrho}$ whose diagonal ensembles have the same support share the same nonempty population index

subset, the opposite implication can be false [i.e., we can have $\mathbb{S}[\hat{\rho}] = \mathbb{S}[\hat{\varrho}]$ but $\mathrm{Supp}[\Phi(\hat{\rho})] \neq \mathrm{Supp}[\Phi(\hat{\varrho})]$].

As will be clear in the next sections, the support space (9) of the diagonal ensemble of a state plays a central role in our analysis. For this reason given $\mathcal{A}$ a (nonempty) linear subset of $\mathcal{H}$, we find it convenient to define $\mathfrak{S}_{\mathcal{A}}$ the set of density matrices $\hat{\rho}$ whose energy diagonal ensemble has support that corresponds to such space, i.e.,

$$\mathfrak{S}_{\mathcal{A}} := \{\hat{\rho} : \mathrm{Supp}[\Phi(\hat{\rho})] = \mathcal{A}\}. \tag{11}$$

By a closed inspection of Eq. (9) it turns out that only nontrivial (i.e., not empty) examples of $\mathfrak{S}_{\mathcal{A}}$ are those where $\mathcal{A}$ is a direct sum of a collection $\{\mathcal{A}_0, \mathcal{A}_1, \ldots, \mathcal{A}_{M-1}\}$ of (possibly empty) linear subsets of the energy eigenspaces of the system Hamiltonian $\hat{H}$, i.e.,

$$\mathcal{A} := \bigoplus_{i=0}^{M-1} \mathcal{A}_i, \quad \mathcal{A}_i \subseteq \mathcal{H}_i. \tag{12}$$

Notice also that while in general the elements of $\mathfrak{S}_{\mathcal{A}}$ could have different spectral decompositions, from Eq. (9) it follows that given

$$\mathbb{S} := \{i : \dim[\mathcal{A}_i] > 0\}, \tag{13}$$

the set which identifies the nonempty elements of $\{\mathcal{A}_0, \mathcal{A}_1, \ldots, \mathcal{A}_{M-1}\}$, we must have

$$\forall\, \hat{\rho} \in \mathfrak{S}_{\mathcal{A}} \Longrightarrow \begin{cases} \mathbb{S}[\hat{\rho}] = \mathbb{S}, \\ \mathcal{H}_i[\Phi(\hat{\rho})] = \mathcal{A}_i\ \forall\, i \in \mathbb{S}. \end{cases} \tag{14}$$

Special instances of the sums (12) are provided by the Hilbert space itself $\mathcal{H} := \bigoplus_{i=0}^{M-1} \mathcal{H}_i$ (in this case $\mathfrak{S}_{\mathcal{H}}$ includes all the states of the model) and by the single-state elements $\mathcal{A}^{[1,j]} := \oplus_{i=1}^{M-1} \mathcal{A}_i^{[1,j]}$ characterized by the fact that their only nontrivial term is the $j$th one which corresponds to a single non-null vector of the $j$th energy eigenspace $\mathcal{H}_j$, so that the associated nonempty elements set is $\mathbb{S} = \{j\}$ and

$$\dim\left[\mathcal{A}_i^{[1,j]}\right] = \delta_{j,i}. \tag{15}$$

Important examples of density matrices which can be found in $\mathfrak{S}_{\mathcal{A}}$ are represented by the Gibbs-like states $\hat{\omega}_{\mathcal{A}}(\beta)$ obtained by taking a thermal state of inverse temperature $\beta \geqslant 0$ and filtering out the energy levels which are not in $\mathcal{A}$, i.e.,

$$\hat{\omega}_{\mathcal{A}}(\beta) := \frac{\hat{\Pi}_{\mathcal{A}} e^{-\beta \hat{H}}}{Z_{\mathcal{A}}(\beta)} = \frac{\sum_{i\in\mathbb{S}} \hat{\Pi}_{\mathcal{A}_i} e^{-\beta \epsilon_i}}{Z_{\mathcal{A}}(\beta)}, \tag{16}$$

with $\hat{\Pi}_{\mathcal{A}_i}$ being the projector on the $i$th block $\mathcal{A}_i$ of $\mathcal{A}$ and with

$$Z_{\mathcal{A}}(\beta) := \mathrm{Tr}[\hat{\Pi}_{\mathcal{A}} e^{-\beta \hat{H}}] = \sum_{i\in\mathbb{S}} e^{-\beta\epsilon_i} \mathrm{Tr}[\hat{\Pi}_{\mathcal{A}_i}], \tag{17}$$

where $\hat{\Pi}_{\mathcal{A}} = \sum_{i\in\mathbb{S}} \hat{\Pi}_{\mathcal{A}_i}$ is the projector on $\mathcal{A}$. We stress that, by construction, the states $\hat{\omega}_{\mathcal{A}}(\beta)$ are invariant under $\Phi$, i.e.,

$$\hat{\omega}_{\mathcal{A}}(\beta) = \Phi(\hat{\omega}_{\mathcal{A}}(\beta)). \tag{18}$$

Notice also that in the high-temperature limit $\beta = 0$, Eq. (16) reduces to the fully mixed state on $\mathcal{A}$, i.e.,

$$\hat{\omega}_{\mathcal{A}}(0) := \frac{\hat{\Pi}_{\mathcal{A}}}{\mathrm{Tr}[\hat{\Pi}_{\mathcal{A}}]}, \tag{19}$$

which is still a proper element of $\mathfrak{S}_{\mathcal{A}}$. On the contrary, in the zero-temperature limit $\beta \to \infty$ of $\hat{\omega}_{\mathcal{A}}(\beta)$, Eq. (16) converges to a state which typically is not in $\mathfrak{S}_{\mathcal{A}}$. Indeed the latter corresponds to the density matrix

$$\lim_{\beta\to\infty} \hat{\omega}_{\mathcal{A}}(\beta) = \hat{\omega}_{\mathcal{A}_{\min}}(0) = \frac{\hat{\Pi}_{\mathcal{A}_{\min}}}{\mathrm{Tr}[\hat{\Pi}_{\mathcal{A}_{\min}}]}, \tag{20}$$

which has support on the restricted subspace $\mathcal{A}_{\min} := \mathcal{A}_{\min_{i\in\mathbb{S}}}$ identified by the nonempty block term of $\mathcal{A}$ that has the smallest energy eigenvalue, i.e.,

$$\epsilon_{\min}(\mathcal{A}) := \min_{i\in\mathbb{S}} \epsilon_i = \epsilon_{\min_{i\in\mathbb{S}}}. \tag{21}$$

We finally introduce a partial ordering on the subspaces (12):

*Definition 1.* Given two direct sums of linear subsets of the energy eigenspace of the system, $\mathcal{A} := \bigoplus_{i=0}^{M-1} \mathcal{A}_i$ and $\mathcal{A}' := \bigoplus_{i=0}^{M-1} \mathcal{A}'_i$, we say that the former is not dominated by the latter (in formulas $\mathcal{A} \succeq \mathcal{A}'$) if there exists a energy-preserving unitary mapping $\hat{V}$ that maps each component of $\mathcal{A}$ into the corresponding element of $\mathcal{A}'$, i.e.,

$$\begin{aligned} \mathcal{A} \succeq \mathcal{A}' \Longleftrightarrow\ & \exists \hat{V}\, \text{unitary}, [\hat{H}, \hat{V}] = 0\ \text{s.t.} \\ & V[\mathcal{A}_i] \subseteq \mathcal{A}'_i, \quad \forall i \in \{0, \ldots, M-1\}, \end{aligned} \tag{22}$$

with $V[\mathcal{A}_i]$ representing the image of $\mathcal{A}_i$ under the action of $\hat{V}$. In case the relation can also be inverted (i.e., if we also have $\mathcal{A}' \succeq \mathcal{A}$) we say that the two sums are equivalent (in formula $\mathcal{A} \approx \mathcal{A}'$). Clearly a necessary and sufficient condition to have that $\mathcal{A}$ is not dominated by $\mathcal{A}'$ is that the sub-blocks of the former have dimensions which are not larger than the corresponding ones of the latter,

$$\mathcal{A} \succeq \mathcal{A}' \Longleftrightarrow \dim[\mathcal{A}_i] \leqslant \dim[\mathcal{A}'_i]\ \forall\, i \in \{0, \ldots, M-1\}. \tag{23}$$

Similarly a necessary and sufficient condition to ensure that $\mathcal{A}$ and $\mathcal{A}'$ are equivalent is instead given by

$$\mathcal{A} \sim \mathcal{A}' \Longleftrightarrow \dim[\mathcal{A}_i] = \dim[\mathcal{A}'_i]\ \forall\, i \in \{0, \ldots, M-1\}. \tag{24}$$

Observe also that for all not trivial $\mathcal{A}$ we can write

$$\mathcal{A}^{[1,j]} \succeq \mathcal{A} \succeq \bar{\mathcal{A}} \succeq \mathcal{H}\ \forall\, j \in \mathbb{S}, \tag{25}$$

where $\mathbb{S}$ is the nonempty elements set of $\mathcal{A}$, $\mathcal{A}^{[1,j]}$ is the single state subset defined in Eq. (15), and finally $\bar{\mathcal{A}}$ is the direct sum obtained by replacing all nonempty elements of $\mathcal{A}$ with the associated energy eigenspaces of $\hat{H}$, i.e.,

$$\bar{\mathcal{A}} := \bigoplus_{i=1}^{M-1} \bar{\mathcal{A}}_i, \quad \bar{\mathcal{A}}_i := \begin{cases} \mathcal{H}_i & \forall\, i \in \mathbb{S}, \\ \varnothing & \forall\, i \notin \mathbb{S}. \end{cases} \tag{26}$$

## III. DETERMINISTIC WORK EXTRACTION

In the two-point measurement (TPM) formalism [14–17] the work we can extract from the state $\hat{\rho}$ of the system through the application of a unitary transformation $\hat{U}$ is determined through the following process: At time $t_{\mathrm{in}}$, before the application of $\hat{U}$, a projective measurement is performed with respect to to the energy projectors $\{\hat{\Pi}_0, \hat{\Pi}_1, \ldots\}$: following the formalism introduced in the previous section, for each $i \in \mathbb{S}[\hat{\rho}]$ there is a nonzero probability $P(i|\hat{\rho})$ that the system will be projected into the density matrix $\hat{\rho}_i$ of Eq. (6), hence setting the input energy of the model at $E_{\mathrm{in}} = \epsilon_i$. The system

is hence evolved through $\hat{U}$ and a second energy measurement is performed at time $t_{\text{out}}$ obtaining the energy value $E_{\text{out}} = \epsilon_j$ with probability

$$P_{\hat{U}}(j|\hat{\rho}_i) := \text{Tr}[\hat{\Pi}_j \hat{U} \hat{\rho}_i \hat{U}^\dagger] = \sum_{k=1}^{r_i} p_i^{(k)} \langle \epsilon_{i,k}|\hat{U}^\dagger \hat{\Pi}_j \hat{U}|\epsilon_{i,k}\rangle. \tag{27}$$

The extracted work is described by the quantity

$$w = E_{\text{in}} - E_{\text{out}}, \tag{28}$$

which happens to be a random variable that can take the discrete values $(\epsilon_i - \epsilon_j)$ with probabilities

$$P_{\hat{\rho};\hat{U}}(j,i) := P(i|\hat{\rho}) P_{\hat{U}}(j|\hat{\rho}_i) = \text{Tr}[\hat{\Pi}_j \hat{U} \hat{\Pi}_i \hat{\rho} \hat{\Pi}_i \hat{U}^\dagger], \tag{29}$$

the corresponding distribution being formally described by the formula

$$P_{\hat{\rho};\hat{U}}^{(\hat{H})}(w) := \sum_{j,i} P_{\hat{\rho};\hat{U}}(j,i) \delta(w - (\epsilon_i - \epsilon_j)). \tag{30}$$

It is important to stress that in the TPM protocol the unitary is fixed a priori and cannot be modified after the acquisition of the first measurement outcome. It is clear that if we do allow for the possibility of adapting the unitary transformation to the measurement outcome we can recover much more energy than we get in the TPM protocol (indeed, at least for models where the Hamiltonian in not degenerate, we can recover the full amount of the energy stored into the system by simply using unitaries $\hat{U}_j$ which maps $|\epsilon_j\rangle$ into the ground state). However in this way we are basically pumping entropy output of the system, which is equivalent to put the system in thermal contact with a zero-temperature bath. Notice also that replacing $\hat{\rho}$ with its energy diagonal part (5) in the left-hand side (l.h.s.) of Eq. (29) the quantity does not change [i.e., $P_{\hat{\rho};\hat{U}}(j,i) = P_{\Phi(\hat{\rho});\hat{U}}(j,i)$]: this implies that for what it concerns the work we can extract from the system via TPM protocols, the states $\hat{\rho}$ and $\Phi(\hat{\rho})$ exhibit the same statistical properties, i.e.,

$$P_{\hat{\rho};\hat{U}}^{(\hat{H})}(w) = P_{\Phi(\hat{\rho});\hat{U}}^{(\hat{H})}(w). \tag{31}$$

Our focus is on the first moment of this distribution, i.e., the quantity

$$\begin{aligned}\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle &:= \int dw P_{\hat{\rho};\hat{U}}^{(\hat{H})}(w) w = \sum_{j,i} P_{\hat{\rho};\hat{U}}(j,i)(\epsilon_i - \epsilon_j) \\ &= \text{Tr}[\hat{H}\hat{\rho}] - \text{Tr}[\hat{H}\hat{U}\Phi(\hat{\rho})\hat{U}^\dagger] \\ &= \text{Tr}[\hat{H}\Phi(\hat{\rho})] - \text{Tr}[\hat{H}\hat{U}\Phi(\hat{\rho})\hat{U}^\dagger],\end{aligned} \tag{32}$$

which represents the mean work we can extract from $\hat{\rho}$ [i.e., $\Phi(\hat{\rho})$] when employing the unitary $\hat{U}$. Its maximum value corresponds to the ergotropy $\mathcal{E}(\Phi(\hat{\rho});\hat{H})$ of $\Phi(\hat{\rho})$ [22,23], i.e.,

$$\langle W_{\text{max}}(\hat{\rho};\hat{H})\rangle := \max_{\hat{U}} \langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle = \mathcal{E}(\Phi(\hat{\rho});\hat{H}), \tag{33}$$

with the optimal $\hat{U}$ which saturates the maximum being the transformation $\hat{U}_\star$ which transforms $\Phi(\hat{\rho})$ into its passive counterpart $\Phi(\hat{\rho})^\downarrow$ [24,25] [by the same token the minimum of $\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle$ corresponds to the anti-ergotropy $\mathcal{E}_A(\Phi(\hat{\rho});\hat{H})$ of the diagonal ensemble state]. Notice that since the passive state energy is a Schur-concave functional [37] it follows that $\mathcal{E}(\Phi(\hat{\rho});\hat{H})$ is always not larger than $\mathcal{E}(\hat{\rho};\hat{H})$, so that

$$\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle \leqslant \mathcal{E}(\Phi(\hat{\rho});\hat{H}) \leqslant \mathcal{E}(\hat{\rho};\hat{H}) \; \forall \, \hat{U}, \tag{34}$$

meaning that the TPM process is less efficient than the ergotropy protocol in extracting energy from the state. We also consider the variance of the extracted work, i.e., the quantity

$$\begin{aligned}\langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle &= \int dw P_{\hat{\rho};\hat{U}}^{(\hat{H})}(w)[w - \langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle]^2 \\ &= \sum_{j,i} P_{\hat{\rho};\hat{U}}(j,i)[(\epsilon_i - \epsilon_j) - \langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle]^2 \\ &= \langle W_{\hat{U}}^2(\hat{\rho};\hat{H})\rangle - \langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle^2.\end{aligned} \tag{35}$$

First notice that for each system there exists always at least a choice of $\hat{U}$ such that $\langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle = 0$ (for instance, $\hat{U} = \hat{I}$). If the associated mean value $W = \langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle$ is non-negative (of course this not the case for $\hat{U} = \hat{I}$), we say that for such unitaries the TPM protocol allows one to extract the work $W$ deterministically, i.e., with zero fluctuations:

*Definition 2.* A work value $W \geqslant 0$ is said to be deterministically extractable from the state $\hat{\rho}$ of the system if there exists a $\hat{U}$ unitary such that

$$P_{\hat{\rho};\hat{U}}^{(\hat{H})}(w) = \delta(w - W), \tag{36}$$

or, equivalently, if and only if

$$\begin{aligned}\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle &= W, \\ \langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle &= 0.\end{aligned} \tag{37}$$

By looking carefully at the definitions we have introduced so far, it is clear the only possible values $W$ that fulfill Eq. (37) are those associated with the non-negative energy gaps of the spectrum of $\hat{H}$. More specifically we can claim that a certain value of work $W \geqslant 0$ can be extracted deterministically from $\hat{\rho}$ if and only if there exists a mapping $\mu : \mathbb{S}[\hat{\rho}] \mapsto \{0, 1, \ldots, M-1\}$ and a unitary evolution $\hat{U}$ such that

$$\forall \, i \in \mathbb{S}[\hat{\rho}] \quad \begin{cases} \epsilon_i - \epsilon_{\mu(i)} = W, \\ P_{\hat{U}}(\mu(i)|\hat{\rho}_i) = 1. \end{cases} \tag{38}$$

Furthermore invoking Eq. (27) we can recast the second condition in Eq. (38) as

$$\begin{aligned}&\sum_{k=1}^{r_i} p_i^{(k)} \langle \epsilon_{i,k}|\hat{U}^\dagger \hat{\Pi}_{\mu(i)} \hat{U}|\epsilon_{i,k}\rangle = 1 \\ &\quad \Longleftrightarrow \langle \epsilon_{i,k}|\hat{U}^\dagger \hat{\Pi}_{\mu(i)} \hat{U}|\epsilon_{i,k}\rangle = 1 \; \forall \, k \in \{1, \ldots, r_i\},\end{aligned} \tag{39}$$

where the second line follows from the fact that the probabilities $p_i^{(k)}$ are all strictly positive. Observe that the resulting expression is equivalent to say that the energy subspace $\mathcal{H}_{\mu(i)}$ must be sufficiently large to contain the full image of the set $\mathcal{H}_i[\Phi(\hat{\rho})]$ defined in Eq. (10). We can hence equivalently write Eq. (38) by saying that $W \geqslant 0$ can be extracted deterministically from $\hat{\rho}$ if and only if there exists a mapping $\mu : \mathbb{S}[\hat{\rho}] \mapsto \{0, 1, \ldots, M-1\}$ and a unitary evolution $\hat{U}$ such that

$$\forall \, i \in \mathbb{S}[\hat{\rho}] \quad \begin{cases} \epsilon_i - \epsilon_{\mu(i)} = W, \\ U[\mathcal{H}_i[\Phi(\hat{\rho})]] = \mathcal{H}_{\mu(i)}, \end{cases} \tag{40}$$

with $U[\mathcal{H}_i[\Phi(\hat{\rho})]]$ being the image of $\mathcal{H}_i[\Phi(\hat{\rho})]$ under the action of $\hat{U}$. The above expression can now be used to establish the following general rules:

*Lemma 1.* Let $\hat{U}$ be a unitary transformation which allows for the deterministic extraction of a work value $W \geqslant 0$ from the state $\hat{\rho}$. Then such unitary will lead the same outcome when applied to any other density matrix $\hat{\varrho}$ whose diagonal ensemble $\Phi(\hat{\varrho})$ has the same support of $\Phi(\hat{\rho})$, i.e.,

$$\mathrm{Supp}[\Phi(\hat{\varrho})] = \mathrm{Supp}[\Phi(\hat{\rho})] \Longrightarrow \begin{cases} \langle W_{\hat{U}}(\hat{\varrho};\hat{H})\rangle = W, \\ \langle \Delta^2 W_{\hat{U}}(\hat{\varrho};\hat{H})\rangle = 0. \end{cases} \tag{41}$$

*Proof.* Since the diagonal ensembles $\Phi(\hat{\varrho})$ and $\Phi(\hat{\rho})$ have the same support it follows that $\mathbb{S}[\hat{\varrho}] = \mathbb{S}[\hat{\rho}]$ and $\mathcal{H}_i[\Phi(\hat{\varrho})] = \mathcal{H}_i[\Phi(\hat{\rho})]$ for all $i \in \mathbb{S}[\hat{\rho}]$. Accordingly, if the condition (40) applies to $\hat{\rho}$ then it also applies to $\hat{\varrho}$. ■

It is worth stressing that Lemma 1 does not requires $\Phi(\hat{\rho})$ and $\Phi(\hat{\varrho})$ to have the same spectrum, it only matters that they have the same support.

*Lemma 2.* Let $\hat{\rho}$ and $\hat{\rho}'$ be two density matrices such that the support of $\Phi(\hat{\rho}')$ can be mapped into the support of $\Phi(\hat{\rho})$ via an energy preserving unitary operation. Then for each $\hat{U}$ unitary transformation which allows for the deterministic extraction of a work value $W \geqslant 0$ from the state $\hat{\rho}$, there exists a new unitary $\hat{U}'$ which allows us to do the same from $\hat{\rho}'$.

*Proof.* Let $\hat{V}$ be the energy preserving unitary transformation that sends $\mathrm{Supp}[\Phi(\hat{\rho}')]$ into $\mathrm{Supp}[\Phi(\hat{\rho})]$. Recalling (9) this implies that for all $i \in \mathbb{S}[\hat{\rho}']$ we must have

$$V[\mathcal{H}_i[\Phi(\hat{\rho}')]] = \mathcal{H}_i[\Phi(\hat{\rho})], \tag{42}$$

where as usual we used $V[\mathcal{H}_i[\Phi(\hat{\rho}')]]$ to indicate the image of $\mathcal{H}_i[\Phi(\hat{\rho}')]$ under $\hat{V}$. The thesis hence follows by observing that if $\hat{U}$ fulfils the deterministic work extraction condition (40) for $\hat{\rho}$, then the unitary $\hat{U}' := \hat{U}\hat{V}$ does the same for $\hat{\rho}'$. ■

In the remaining of the present paper we focus on the characterization of the maximum work that can be deterministically extracted from a given input state:

*Definition 3.* The maximum deterministic extractable work (MDEW) of a state $\hat{\rho}$ is the maximum value of the values $W$ which fulfill the condition (37), i.e., the quantity

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) := \max_{\hat{U}} \{\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle : \langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle = 0\}. \tag{43}$$

Clearly the configurations for which one expects MDEW to be strictly positive correspond to *rare events*: this is a consequence of the fact that even the smallest perturbation in the spectrum of $\hat{H}$ or in the support of $\hat{\rho}$ will tend to assign a positive value to the TPM work variance functional $\langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle$ [for instance in the case of the example of Eq. (46) discussed below, it is sufficient to take $\epsilon_1 = E$, $\epsilon_2 = 2E(1+\delta)$ with $\delta > 0$, or to add a small but nonzero population to the ground state of $\hat{\rho}$, to get $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = 0$]. Nonetheless the study of $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H})$ can give us some hint on the efficiency of work extraction procedures in many cases of practical interests where geometrical or symmetry properties bound the system to assume assigned spectral characteristic.

## IV. PRELIMINARY OBSERVATIONS

It also goes without mentioning that $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H})$ coincides with $W_{\max}^{(\mathrm{det})}(\Phi(\hat{\rho});\hat{H})$ and that, thanks to (33), it is upper bounded by $\mathcal{E}(\Phi(\hat{\rho});\hat{H})$, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = W_{\max}^{(\mathrm{det})}(\Phi(\hat{\rho});\hat{H}) \leqslant \mathcal{E}(\Phi(\hat{\rho});\hat{H}). \tag{44}$$

As a direct consequence of this fact, it follows that if $\Phi(\hat{\rho})$ is a passive state, then $\langle W_{\max}(\hat{\rho};\hat{H})\rangle = 0$ with the optimal unitary $\hat{U}_\star$ being the identity operator; accordingly we have that the maximum of the deterministic work of these states is simply zero, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = 0 \;\forall\; \Phi(\hat{\rho}) \text{ passive}. \tag{45}$$

Another case in which the MDEW can be easily computed is when $\Phi(\hat{\rho})$ is pure, i.e., when such a state, and hence $\hat{\rho}$, corresponds to the an eigenvector of $\hat{H}$: under this circumstance the maximum deterministic work we can get corresponds to the ergotropy which incidentally corresponds to the mean energy of the state, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = \mathrm{Tr}[\hat{H}\hat{\rho}] \;\forall\; \Phi(\hat{\rho}) \text{ pure}. \tag{46}$$

A less trivial example is provided by the following configuration: let $\hat{H} = \epsilon_2|\epsilon_2\rangle\langle\epsilon_2| + \epsilon_1|\epsilon_1\rangle\langle\epsilon_1|$ be a nondegenerate, three level Hamiltonian with uniforms energy gaps, i.e., $\epsilon_1 = E$, $\epsilon_2 = 2E$. For any rank-2 density matrix $\Phi(\hat{\rho})$ with support space $\mathrm{Span}\{|\epsilon_1\rangle, |\epsilon_2\rangle\}$ we can then write

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = E. \tag{47}$$

The same holds if the matrix has rank-1 with nonzero population on $|\epsilon_1\rangle$, while if it has rank-1 but nonzero population on $|\epsilon_2\rangle$ we get $W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = 2E$. To see this observe using the unitary $\hat{U} := |\epsilon_1\rangle\langle\epsilon_2| + |\epsilon_0\rangle\langle\epsilon_1| + |\epsilon_2\rangle\langle\epsilon_0|$ we can induce the transitions $|\epsilon_1\rangle \mapsto |\epsilon_0\rangle$ and $|\epsilon_2\rangle \mapsto |\epsilon_1\rangle$ which both yield exactly the work value $\Delta$. To get more than this one would need necessarily to couple $|\epsilon_2\rangle$ with $|\epsilon_0\rangle$: such amount of work however cannot be matched by any transitions that involves $|\epsilon_1\rangle$ as input state. As a result these type of operations will involve random outcomes leading to nonzero values of $\langle \Delta^2 W_{\hat{U}}(\hat{\rho};\hat{H})\rangle$. Notice finally that, as a consequence of Lemma 1, (46) holds true irrespectively from the specific values of the populations of the level $|\epsilon_2\rangle$ and $|\epsilon_1\rangle$. This is a general rule that, recalling the definitions of $\mathcal{A}$ and $\mathfrak{S}_{\mathcal{A}}$ introduced in Sec. II, can be summarized as follows:

*Corollary 1.* All inputs states $\hat{\rho}$ of the set $\mathfrak{S}_{\mathcal{A}}$ share the same MDEW value, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\rho};\hat{H}) = W_{\max}^{(\mathrm{det})}(\mathcal{A};\hat{H}) \;\forall\; \hat{\rho} \in \mathfrak{S}_{\mathcal{A}}, \tag{48}$$

where recalling that $\hat{\omega}_{\mathcal{A}}(0)$ of Eq. (19) belongs to $\mathfrak{S}_{\mathcal{A}}$ we can identify the constant $W_{\max}^{(\mathrm{det})}(\mathcal{A};\hat{H})$ as

$$W_{\max}^{(\mathrm{det})}(\mathcal{A};\hat{H}) := W_{\max}^{(\mathrm{det})}(\hat{\omega}_{\mathcal{A}}(0);\hat{H}). \tag{49}$$

Furthermore, irrespectively from the selected input state, such optimal value can be obtained using the same optimal unitary transformation $\hat{U}_\star$, i.e.,

$$\begin{aligned} &\langle W_{\hat{U}_\star}(\hat{\rho};\hat{H})\rangle = W_{\max}^{(\mathrm{det})}(\mathcal{A};\hat{H}), \\ &\langle \Delta^2 W_{\hat{U}_\star}(\hat{\rho};\hat{H})\rangle = 0, \end{aligned} \quad \forall\; \hat{\rho} \in \mathfrak{S}_{\mathcal{A}}. \tag{50}$$

*Proof.* Use Lemma 1 and the fact that the elements of $\mathfrak{S}_{\mathcal{A}}$ share the same support space $\mathcal{A}$. ■

In a similar way follows Corollary 2:

*Corollary 2.* Let $\mathcal{A}$ and $\mathcal{A}'$ be two equivalent (nontrivial) direct sums of linear subset of the energy eigenspaces of the system. Then the MDEW values $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ and $W_{\max}^{(\det)}(\mathcal{A}';\hat{H})$ associated with the states of the sets $\mathfrak{S}_{\mathcal{A}}$ and $\mathfrak{S}_{\mathcal{A}'}$ coincide, i.e.,

$$\mathcal{A}\sim\mathcal{A}' \Longrightarrow W_{\max}^{(\det)}(\mathcal{A};\hat{H}) = W_{\max}^{(\det)}(\mathcal{A}';\hat{H}). \tag{51}$$

*Proof.* Use Lemma 2 and the fact that, according to Definition 1, the support spaces $\mathcal{A}$ and $\mathcal{A}'$ of the density matrices of $\mathfrak{S}_{\mathcal{A}}$ and $\mathfrak{S}_{\mathcal{A}'}$ are connected by energy preserving unitary transformations that maps the first into the second and vice versa. ■

The above results imply that, a part from the energy eigenvalues of $\hat{H}$, the MDEW value $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ can only depend on the dimensions of the sub-blocks of $\mathcal{A}$. Accordingly we can always express $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ as a function $\mathcal{W}(\vec{r}(\mathcal{A}),\vec{\epsilon}\,)$ of the vectors $\vec{\epsilon} := (\epsilon_0,\ldots,\epsilon_{M-1})$ and $\vec{r}(\mathcal{A}) := (\dim[\mathcal{A}_0],\ldots,\dim[\mathcal{A}_{M-1}])$. As a special example note that in the case of the single-state elements (15) from Eq. (46) we get

$$W_{\max}^{(\det)}(\mathcal{A}^{[1,j]};\hat{H}) = \mathcal{W}(\vec{r}[\mathcal{A}^{[1,j]}],\vec{\epsilon}) = \vec{r}[\mathcal{A}^{[1,j]}]\cdot\vec{\epsilon} = \epsilon_i, \tag{52}$$

while, recalling that all passive states have maximum rank and hence belong to $\mathfrak{S}_{\mathcal{H}}$ we can rewrite (45) as

$$\mathcal{W}(\vec{r}(\mathcal{H}),\vec{\epsilon}\,) = 0. \tag{53}$$

We next observe that the partial ordering (22) introduced in Definition 1 can be used to rank the values of the function $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$:

*Lemma 3.* Let $\mathcal{A}$ and $\mathcal{A}'$ be two (nontrivial) direct sums of linear subset of the energy eigenspaces of the system. If $\mathcal{A}$ is not dominated by $\mathcal{A}'$ then the MDEW value $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ is larger than or equal to $W_{\max}^{(\det)}(\mathcal{A}';\hat{H})$, i.e.,

$$\mathcal{A}\succeq\mathcal{A}' \Longrightarrow W_{\max}^{(\det)}(\mathcal{A};\hat{H}) \geqslant W_{\max}^{(\det)}(\mathcal{A}';\hat{H}). \tag{54}$$

*Proof.* According to (22) there exists an energy-preserving unitary transformation $\hat{V}$ that maps the $i$th subspace of $\mathcal{A}$ into the corresponding one of $\mathcal{A}'$. Let now $\hat{U}'_\star$ be the optimal unitary map which applied to a generic states of $\mathfrak{S}_{\mathcal{A}'}$ enable us to extract the work value $W_{\max}^{(\det)}(\mathcal{A}';\hat{H})$ from the system. The thesis then follows by observing that the unitary $\hat{U}'_\star\hat{V}$ applied to the elements of $\mathfrak{S}_{\mathcal{A}}$ enable the deterministic extraction of the work level $W_{\max}^{(\det)}(\mathcal{A}';\hat{H})$, which hence, by construction is a lower bound of the MDEW we can get from $\mathfrak{S}_{\mathcal{A}}$. ■

In particular from (25) we get the following bounds

$$\epsilon_i \geqslant W_{\max}^{(\det)}(\mathcal{A};\hat{H}) \geqslant W_{\max}^{(\det)}(\bar{\mathcal{A}};\hat{H}) \geqslant 0\ \forall\, i\in\mathbb{S}, \tag{55}$$

where in writing the leftmost and rightmost terms we used the identities (52) and (53) respectively.

The dependence of $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ with respect to the spectrum of $\hat{H}$ for fixed choices of $\mathcal{A}$ is slightly more involved and, as will be discussed in Sec. VI, can lead to unexpected results.

## V. SUPERADDITIVITY PROPERTIES AND THE ASYMPTOTIC MAXIMUM DETERMINISTIC EXTRACTABLE WORK RATIO

Consider next the case where we have $n$ copies of the input state $\hat{\rho}$ for a system where the global Hamiltonian is composed by a sum $\hat{H}^{(n)} := \sum_{k=1}^{n}\hat{H}_k$ of homogeneous local terms ($\hat{H}_k$ being the local Hamiltonian of the $k$th copy). We are interested in determining how the $n$-copies MDEW, i.e., the quantity $W_{\max}^{(\det)}(\hat{\rho}^{\otimes n};\hat{H}^{(n)})$, scales with $n$. Let us start with some preliminary observations. First of all, notice that, due to the absence of interaction among the various copies of the system, the $n$-uses energy decoherence LCPTP map of the model correspond to the $n$ copies of the map $\Phi$ of Eq. (2), i.e., $\Phi^{(n)} = \Phi^{\otimes n}$. From this it hence follows that if $\mathcal{A}$ is the support space of $\Phi(\hat{\rho})$ then $\mathcal{A}^{\otimes n}$ is the support of $\Phi^{(n)}(\hat{\rho}^{\otimes n}) = \Phi(\hat{\rho})^{\otimes n}$, i.e.,

$$\hat{\rho}\in\mathfrak{S}_{\mathcal{A}} \Longrightarrow \hat{\rho}^{\otimes n}\in\mathfrak{S}_{\mathcal{A}^{\otimes n}}. \tag{56}$$

From Eqs. (48) and (49) we can thus conclude that

$$W_{\max}^{(\det)}(\hat{\rho}^{\otimes n};\hat{H}^{(n)}) = W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)})\ \forall\,\hat{\rho}\in\mathfrak{S}_{\mathcal{A}}, \tag{57}$$

with

$$\begin{aligned} W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)}) &= W_{\max}^{(\det)}(\hat{\omega}_{\mathcal{A}^{\otimes n}}(0);\hat{H}^{(n)}) \\ &= W_{\max}^{(\det)}\big(\hat{\omega}_{\mathcal{A}}^{\otimes n}(0);\hat{H}^{(n)}\big), \end{aligned} \tag{58}$$

where in the second line we used the identity $\hat{\omega}_{\mathcal{A}^{\otimes n}}(0) = \hat{\omega}_{\mathcal{A}}^{\otimes n}(0)$. We can then arrive to the following inequality:

$$W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)}) \geqslant nW_{\max}^{(\det)}(\mathcal{A};\hat{H}), \tag{59}$$

by observing that if there exists a unitary procedure that extracts deterministic work $W_{\max}^{(\det)}(\mathcal{A};\hat{H})$ from a single copy of a state [say $\hat{\omega}_{\mathcal{A}}(0)$] we can simply reiterate it to extract $n$ times such quantity from $n$ copy of the same density matrix [i.e., from $\hat{\omega}_{\mathcal{A}}^{\otimes n}(0)$]. On the contrary, there are examples which show that the gap in Eq. (59) is nonzero. For instance adding an extra energy level $|-1\rangle$ with energy $-\delta$ to the example of Eq. (46), it turns out that as long as $\delta$ is positive and $\neq\Delta$, from $\hat{\rho}^{\otimes 2}$ we can extract energy $2\Delta+\delta > 2\Delta$ which is larger than twice the max value we can get from a single copy of $\hat{\rho}$. Using the same argument we can also conclude that for all $n$, $k$ integers the following superadditivity rule holds:

$$\begin{aligned} W_{\max}^{(\det)}(\mathcal{A}^{\otimes(n+k)};\hat{H}^{(n+k)}) &\geqslant W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)}) \\ &\quad + W_{\max}^{(\det)}(\mathcal{A}^{\otimes k};\hat{H}^{(k)}). \end{aligned} \tag{60}$$

A slightly less trivial observation is that there exist models for which, even though $W_{\max}^{(\det)}(\mathcal{A};\hat{H}) = 0$, for sufficiently large $n$ one has $W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)}) > 0$. From now on we call this the *strong superadditivity* property of the maximum deterministic TPM work. Motivated by this observation we define the asymptotic MDEW ratio as

$$\mathcal{R}(\mathcal{A};\hat{H}) := \limsup_{n\to\infty}\mathcal{R}_n(\mathcal{A};\hat{H}), \tag{61}$$

with

$$\begin{aligned} \mathcal{R}_n(\mathcal{A};\hat{H}) &:= \frac{W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)})}{n} \\ &= W_{\max}^{(\det)}(\mathcal{A}^{\otimes n};\hat{H}^{(n)}/n). \end{aligned} \tag{62}$$

From Eq. (60) it follows that $\mathcal{R}_n(\mathcal{A};\hat{H})$ while not necessarily monotonically increasing is weakly increasing [38], meaning that, even if oscillating it still admits a proper $\to\infty$ limit, i.e.,

$$\begin{aligned} \lim_{n\to\infty}\mathcal{R}_n(\mathcal{A};\hat{H}) &= \limsup_{n\to\infty}\mathcal{R}_n(\mathcal{A};\hat{H}) \\ &= \mathcal{R}(\mathcal{A};\hat{H}) := \max_n \mathcal{R}_n(\mathcal{A};\hat{H}). \end{aligned} \tag{63}$$

### Upper bounds

A natural upper bound for $\mathcal{R}(\mathcal{A};\hat{H})$ [and hence for all $\mathcal{R}_n(\mathcal{A};\hat{H})$] is provided by the minimal energy eigenvalue $\epsilon_{\min}(\mathcal{A})$ of Eq. (21) associated with $\mathcal{A}$, i.e.,

$$\mathcal{R}(\mathcal{A};\hat{H}) \leqslant \epsilon_{\min}(\mathcal{A}). \tag{64}$$

This formally follows from Eq. (55) by taking the minimum with respect to all possible choices of $\epsilon_i$. More intuitively the bound (64) can be explained by that fact that (i) for all $n$, $\hat{\Pi}_{\mathcal{A}}^{\otimes n}$ has a nonzero overlap with the $n$-fold copy of such level, and (ii) we cannot extract more than $n\epsilon_{\min}(\mathcal{A})$ energy from such configuration. Equation (61) establishes that the results of Ref. [31] cannot be used to provide a full characterization of $\mathcal{R}(\mathcal{A};\hat{H})$. Notice also that, as a consequence of (64) it follows that if $\mathbb{S}[\mathcal{A}]$ contains the ground-state energy level then the associated asymptotic ratio is zero, i.e.,

$$0 \in \mathbb{S} \Longrightarrow \mathcal{R}(\mathcal{A};\hat{H}) = \mathcal{R}_n(\mathcal{A};\hat{H}) = 0. \tag{65}$$

An improvement with respect to (64) can be obtained invoking (44), which for $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$ allows us to write

$$\begin{aligned}\mathcal{R}_n(\mathcal{A};\hat{H}) &= \frac{W_{\max}^{(\mathrm{det})}(\hat{\rho}^{\otimes n};\hat{H}^{(n)})}{n} \leqslant \frac{\mathcal{E}(\Phi(\hat{\rho})^{\otimes n};\hat{H}^{(n)})}{n} \\ &\leqslant \limsup_{n\to\infty} \frac{\mathcal{E}(\Phi(\hat{\rho})^{\otimes n};\hat{H}^{(n)})}{n} =: \mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho});\hat{H}),\end{aligned} \tag{66}$$

where $\mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho});\hat{H})$ is the total ergotropy of the state $\Phi(\hat{\rho})$ [22,23]. Taking the minimum of the last term over all possible choices of $\hat{\rho}$, and taking the $n \to \infty$ limit, finally allows us to write

$$\mathcal{R}_n(\mathcal{A};\hat{H}) \leqslant \min_{\hat{\rho}\in\mathfrak{S}_{\mathcal{A}}} \mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho});\hat{H}). \tag{67}$$

Recall next that the Gibbs-like states (16) are special instance of elements of $\mathfrak{S}_{\mathcal{A}}$: therefore a simplified yet in principle less performant version of (67) is given by

$$\mathcal{R}(\mathcal{A};\hat{H}) \leqslant \min_{\beta>0} \mathcal{E}_{\mathrm{tot}}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H}). \tag{68}$$

Written in this form it is now easy to verify that (68) [and hence (67)] implies (64): indeed taking the limit for $\beta \to \infty$ and invoking Eq. (20) we can claim that $\mathcal{R}(\mathcal{A};\hat{H})$ is upper bounded by the total ergotropy of $\hat{\omega}_{\mathcal{A}_{\min}}(0)$ which in turns cannot be larger than mean energy $\epsilon_{\min}(\mathcal{A})$ of such a state. Most importantly, as shown in Appendix A, at least in the case in which $\hat{H}$ has no degenerate spectrum on $\mathcal{A}$ (i.e., when for all $i \in \mathbb{S}$ the projectors $\hat{\Pi}_{\mathcal{A}_i}$ are rank-one operators), it is possible to show that the right-hand side (r.h.s.) of (67) and (68) coincide. Furthermore, in Appendix B we show that the value of $\beta$ that realizes the minimum (68) satisfies the special property

$$S(\hat{\omega}_{\mathcal{A}}(\beta)) = S(\hat{\tau}_\beta), \qquad \hat{\tau}_\beta := \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}[e^{-\beta\hat{H}}]}, \tag{69}$$

where $S(\cdots) := \mathrm{Tr}[(\cdots)\ln(\cdots)]$ is the von Neumann entropy functional and $\hat{\tau}_\beta$ is the thermal Gibbs state of the model with inverse temperature $\beta$. A comparison between $\mathcal{R}_n(\mathcal{A};\hat{H})$ and the upper bound (67) is presented in Fig. 1 for the family of three-level systems (which is unique up to rescaling), and in Figs. 2 and 3 for two distinct families of four-level systems. We remark that the rate of convergence of $\mathcal{R}_n(\mathcal{A};\hat{H})$ to its asymptotic value $\mathcal{R}(\mathcal{A};\hat{H})$ [which we conjecture to coincide with (67)] does depend on the complexity of the fraction, with a simple fraction converging more quickly.

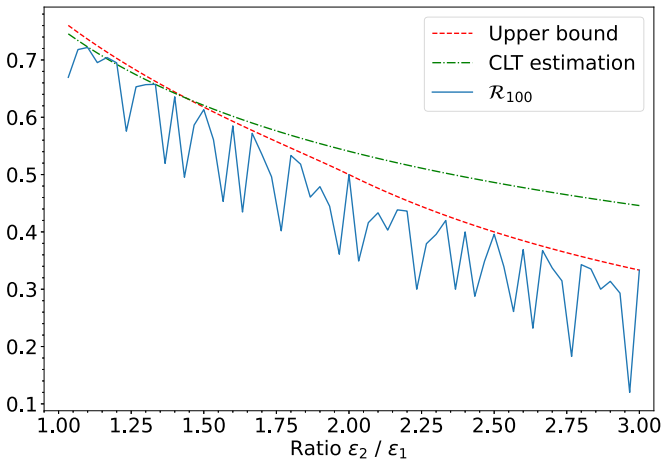


FIG. 1. Values of $\mathcal{R}_n(\mathcal{A};\hat{H})/\epsilon_{d-1}$ for a three-level Hamiltonian $\hat{H} = \epsilon_1 |1\rangle\langle 1| + \epsilon_2 |2\rangle\langle 2|$, for $\mathcal{A} = \mathrm{Span}\{|1\rangle, |2\rangle\}$ as a function of the (rational) value of the energy ratio $\epsilon_2/\epsilon_1 > 1$ (shown every 0.1). Fixing $n = 100$, the finite-size rates $\mathcal{R}_n(\mathcal{A};\hat{H})$ are compared with the upper bound (67) and with the heuristic estimation (163) based on the central limit theorem presented in Sec. IX.

## VI. EXAMPLES

In this section we present some simple (yet nontrivial) examples: these configurations serve as an ideal setting to explore the superadditivity effect outlined in Sec. V, while also facilitating the development of a deeper physical intuition for the problem at hand.

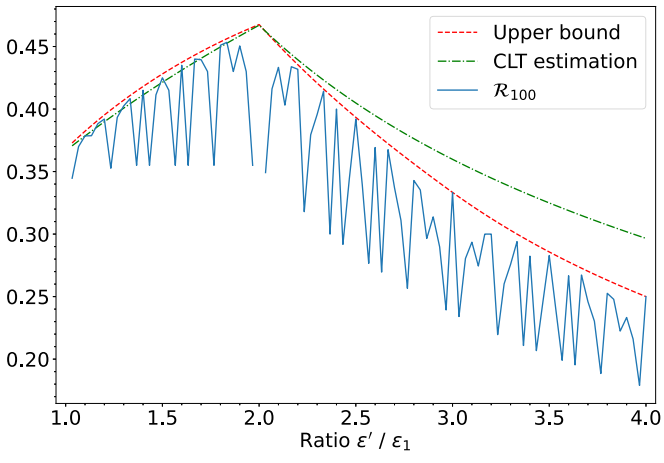


FIG. 2. Values of $\mathcal{R}_n(\mathcal{A};\hat{H})/\epsilon_{d-1}$ for a four-level Hamiltonian $\hat{H} = \epsilon_1 |1\rangle\langle 1| + \frac{3}{2}\epsilon_1 |2\rangle\langle 2| + \epsilon' |3\rangle\langle 3|$, for $\mathcal{A} = \mathrm{Span}\{|1\rangle, |2\rangle, |3\rangle\}$ as a function of the rational value of the energy ratio $\epsilon'/\epsilon_1 > 1$ (shown every 0.1). Fixing $n = 100$, the finite-size rates $\mathcal{R}_n(\mathcal{A};\hat{H})$ are compared with the upper bound (67) and with the heuristic estimation (163) based on the central limit theorem presented in Sec. IX.

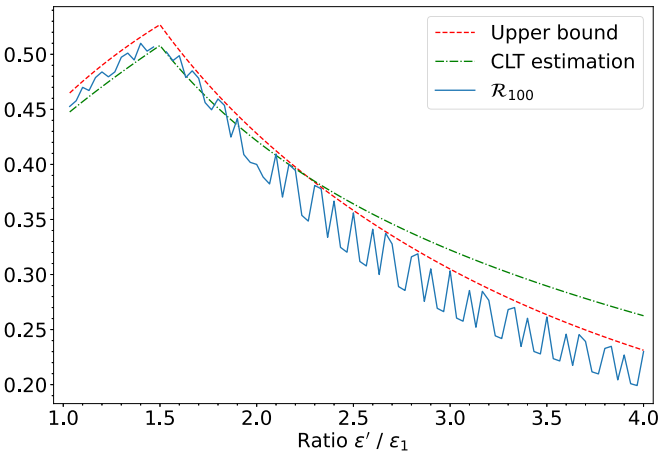


FIG. 3. Values of $\mathcal{R}_n(\mathcal{A};\hat{H})/\epsilon_{d-1}$ for a four-level Hamiltonian $\hat{H} = \epsilon_1 |1\rangle\langle 1| + \epsilon_2 |2\rangle\langle 2|$, for $\mathcal{A} = \mathrm{Span}\{|1\rangle, |2\rangle\}$ as a function of the (rational) value of the second energy level $\epsilon_2 > 1$ (shown every 0.1). Fixing $n = 100$, the finite-size rates $\mathcal{R}_n(\mathcal{A};\hat{H})$ are compared with the upper bound (67) and with the heuristic estimation (163) based on the central limit theorem presented in Sec. IX.

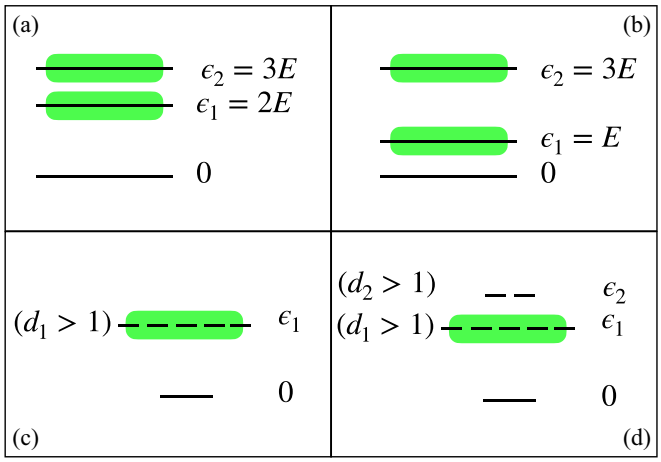


FIG. 4. Schematic representation of the examples analyzed in Sec. VI. Panels (a) and (b) describe the nondegenerate three-level models of Eqs. (73) and (78). Panel (c) describes two-level model of Eqs. (86) with nontrivial degeneracy associated with $\epsilon_1$. Finally, panel (d) describe a three-level model with nontrivial degeneracies for both $\epsilon_1$ and $\epsilon_2$, in which however the highest one is not occupied. In all the examples the green band indicate that the associated level is initially occupied by the input state.

### A. Nondegenerate three-level systems

The simplest nontrivial model we can think of is a nondegenerate three-level system Hamiltonian

$$\hat{H} = \sum_{i=0}^{2} \epsilon_i |\epsilon_i\rangle\langle\epsilon_i|, \tag{70}$$

with input states $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$ which assign nonzero population to just the two top-most energy levels, i.e.,

$$\mathcal{A} = \mathrm{Span}\{|\epsilon_1\rangle, |\epsilon_2\rangle\} = \mathcal{H}_1 \oplus \mathcal{H}_2, \quad \mathbb{S} = \{1, 2\}, \tag{71}$$

so that

$$\hat{\omega}_{\mathcal{A}}(0) = \tfrac{1}{2}(|\epsilon_1\rangle\langle\epsilon_1| + |\epsilon_2\rangle\langle\epsilon_2|). \tag{72}$$

A first example of strong-superadditivity of the MDEW is obtained by setting

$$\epsilon_2 = 3E, \quad \epsilon_1 = 2E, \quad \epsilon_0 = 0, \tag{73}$$

$E > 0$ being a fixed constant [see Fig. 4(a)]. It is easy to check that under this condition the maximum deterministic work we can get from a single copy of $\hat{\omega}_{\mathcal{A}}(0)$ is zero, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\omega}_{\mathcal{A}}(0);\hat{H}) = 0 \Longrightarrow \mathcal{R}_1(\mathcal{A};\hat{H}) = 0. \tag{74}$$

Indeed, the only value of $W$ which fulfils (40) for $i = 1$ is $2E$, which is not acceptable for $i = 2$. Nonetheless it turns out that already for $n = 2$ one has

$$W_{\max}^{(\mathrm{det})}\big(\omega_{\mathcal{A}}^{\otimes 2}(0);\hat{H}^{(2)}\big) = 2E \Longrightarrow R_2(\mathcal{A},\hat{H}) = E. \tag{75}$$

This result can be obtained employing a nonlocal unitary $\hat{U}^{(2)}$ that induces the following transitions on the populated energy levels,

$$\begin{aligned}
|22\rangle &\longrightarrow |11\rangle \quad (W = E + E = 2E),\\
|21\rangle &\longrightarrow |20\rangle \quad (W = 0 + 2E = 2E),\\
|12\rangle &\longrightarrow |02\rangle \quad (W = 2E + 0 = 2E),\\
|11\rangle &\longrightarrow |10\rangle \quad (W = 0 + 2E = 2E),
\end{aligned} \tag{76}$$

where hereafter we use the shorthand notation $|ij\rangle$ to represent the state $|\epsilon_i\rangle \otimes |\epsilon_j\rangle$. To see that this is the optimal solution for $n = 2$ notice that according (40), the only two admissible values of $W$ associated with the energy level $|11\rangle$, are $2E$ [attained in Eq. (76)] and $4E$ (reachable, e.g., through a unitary that maps $|11\rangle$ into $|00\rangle$). The last possibility however is not acceptable since there are no unitary transitions of (say) $|21\rangle$ that could lead to such energy gain [indeed for such level the only admissible values of $W$ compatible with (40) are $E$, $2E$, $3E$, and $5E$]. In a similar fashion one can show that using the three-body unitary $U^{(3)}$ that induces the mapping

$$\begin{aligned}
|222\rangle &\longrightarrow |201\rangle \quad (W = 0 + 3E + E = 4E),\\
|221\rangle &\longrightarrow |101\rangle \quad (W = E + 3E + 0 = 4E),\\
|212\rangle &\longrightarrow |011\rangle \quad (W = 3E + 0 + E = 4E),\\
|122\rangle &\longrightarrow |110\rangle \quad (W = 0 + E + 3E = 4E),\\
|211\rangle &\longrightarrow |200\rangle \quad (W = 0 + 2E + 2E = 4E),\\
|121\rangle &\longrightarrow |020\rangle \quad (W = 2E + 0 + 2E = 4E),\\
|112\rangle &\longrightarrow |002\rangle \quad (W = 2E + 2E + 0 = 4E),\\
|111\rangle &\longrightarrow |100\rangle \quad (W = 0 + 2E + 2E = 4E).
\end{aligned} \tag{77}$$

We get

$$W_{\max}^{(\mathrm{det})}\big(\omega_{\mathcal{A}}^{\otimes 3}(0);\hat{H}^{(3)}\big) = 4E \Longrightarrow R_3(\mathcal{A},\hat{H}) = \frac{4E}{3},$$

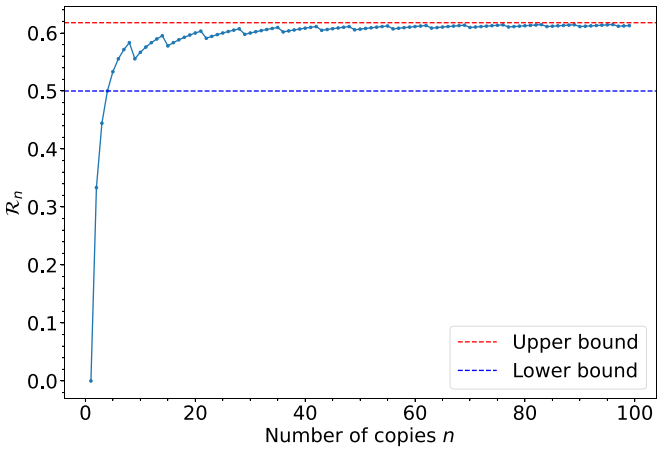


FIG. 5. MDEW rate $R_n(\mathcal{A}, \hat{H})$ for the Hamiltonian model (73). The red dashed line corresponds to the upper bound (68) while the blue dashed line to the lower bound (122) introduced in Sec. VII.

which further improves the MDEW ratio reported in Eq. (75). A numerical study of $R_n(\mathcal{A}, \hat{H})$ for larger values of $n$ is presented in Fig. 5: as evident from the plot in this case, for large $n$ the MDWE ratio approaches the upper bound (68).

A class of models (70) for which the asymptotic ratio $R(\mathcal{A}, \hat{H})$ can be explicitly computed is obtained by setting

$$\epsilon_2 = 3E, \quad \epsilon_1 = E, \quad \epsilon_0 = 0, \tag{78}$$

see Fig. 4(b). Notice that in this case the energy gap $\epsilon_1 - \epsilon_0 = E$ is *half* of the energy gap $\epsilon_2 - \epsilon_1 = 2E$, while in the previous example it was exactly the opposite. Notice also that for $\mathcal{A}$ as in Eq. (71) the upper bound Eq. (64) implies

$$\mathcal{R}(\mathcal{A}^{\otimes n}; \hat{H}^{(n)}) \leqslant \mathcal{R}(\mathcal{A}; \hat{H}) \leqslant E. \tag{79}$$

It is easy to see that similarly to the model of Eq. (72), also in this case we have

$$W_{\max}^{(\mathrm{det})}(\hat{\omega}_{\mathcal{A}}(0); \hat{H}) = 0. \tag{80}$$

For $n = 2$ we get the same result, i.e.,

$$W_{\max}^{(\mathrm{det})}\big(\hat{\omega}_{\mathcal{A}}^{\otimes 2}(0); \hat{H}^{(2)}\big) = 0. \tag{81}$$

To see this notice that here from $|11\rangle$ we have only two possible transitions: toward $|10\rangle$ or $|01\rangle$ which corresponds to the extraction of an energy $E$, or toward $|00\rangle$ with extraction of energy $2E$. From the doublet $|12\rangle$, $|21\rangle$ we have only two possibility: either a transition toward $|02\rangle$, $|20\rangle$ with energy $E$, or a transition toward $|01\rangle$, $|10\rangle$ with energy extraction of $3E$. So we have a match for $E$. However there are no transitions for $|22\rangle$ that produces such an amount of the energy (the minimum energy we can extract from such level is indeed $2E$). What about $n = 3$? In this case we observe that the bound (79) gets saturated, i.e.,

$$W_{\max}^{(\mathrm{det})}\big(\hat{\omega}_{\mathcal{A}}^{\otimes 3}(0); \hat{H}^{(3)}\big) = 3E \Longrightarrow R_3(\mathcal{A}; \hat{H}) = E, \tag{82}$$

implying that $E$ is the asymptotic MDEW ratio of the model. The result of Eq. (82) is achieved with the choice of the unitary $\hat{U}^{(3)}$ which induces the mappings

$$\begin{aligned}
|222\rangle &\longrightarrow |220\rangle \quad (W = 0 + 0 + 3E = 3E),\\
|221\rangle &\longrightarrow |021\rangle \quad (W = 3E + 0 + 0 = 3E),\\
|212\rangle &\longrightarrow |210\rangle \quad (W = 0 + 0 + 3E = 3E),\\
|122\rangle &\longrightarrow |102\rangle \quad (W = 0 + 3E + 0 = 3E),\\
|211\rangle &\longrightarrow |011\rangle \quad (W = 3E + 0 + 0 = 3E),\\
|121\rangle &\longrightarrow |101\rangle \quad (W = 0 + 3E + 0 = 3E),\\
|112\rangle &\longrightarrow |110\rangle \quad (W = 0 + 0 + 3E = 3E),\\
|111\rangle &\longrightarrow |000\rangle \quad (W = E + E + E = 3E).
\end{aligned} \tag{83}$$

Equation (82) can be extended to the whole class of energy spectra of the form

$$\epsilon_2 = NE, \quad \epsilon_1 = E, \quad \epsilon_0 = 0, \tag{84}$$

with $N \geqslant 2$ integer. To see this take $n = N$ and use the unitary $\hat{U}^{(N)}$ which induces the mapping

$$\begin{aligned}
|22\cdots22\rangle &\longrightarrow |02\cdots22\rangle \quad (W = NE + 0 + \cdots + 0 = NE),\\
|22\cdots21\rangle &\longrightarrow |02\cdots21\rangle \quad (W = NE + 0 + \cdots + 0 = NE),\\
&\textit{permutations}\\
|22\cdots211\rangle &\longrightarrow |02\cdots211\rangle (W = NE + 0 + \cdots + 0 = NE),\\
&\textit{permutations}\\
&\vdots\\
|11\cdots11\rangle &\longrightarrow |00\cdots00\rangle \quad (W = E + E + \cdots + E = NE).
\end{aligned}$$

In other words, $\hat{U}^{(N)}$ maps $|11\cdots11\rangle$ into the ground while when acting any other eigenvector of $\hat{\omega}_{\mathcal{A}}^{\otimes N}(0)$ replace one (and only one) of the two terms with a zero. By construction we have that

$$W_{\max}^{(\mathrm{det})}\big(\hat{\omega}_{\mathcal{A}}^{\otimes N}(0); \hat{H}^{(N)}\big) = NE \Longrightarrow R_N(\mathcal{A}; \hat{H}) = E, \tag{85}$$

which once more saturates the bound (64).

### B. Degenerate two-level models

Adding degeneracy in the model typically increases the complexity of the MDEW analysis. Consider, for instance a two-level model with degeneracy $d_1 > 1$ for the excited level $\epsilon_1$ and with the ground level $\epsilon_0 = 0$ that has no degeneracy, i.e.,

$$\hat{H} = \epsilon_1 \sum_{j=0}^{d_1-1} |\epsilon_{1,j}\rangle\langle\epsilon_{1,j}|, \tag{86}$$

with input states $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$ which assign nonzero population to all the elements of the excited level leaving the ground level empty, i.e.,

$$\mathcal{A} = \mathrm{Span}\{|\epsilon_{1,0}\rangle, \ldots, |\epsilon_{1,d_1-1}\rangle\} = \mathcal{H}_1, \quad \mathbb{S} = \{1\}, \tag{87}$$

see Fig. 4(c). Clearly for $n = 1$ we have that no energy can be extracted in the absence of fluctuations, i.e.,

$$W_{\max}^{(\mathrm{det})}(\hat{\omega}_{\mathcal{A}}(0); \hat{H}) = 0 \Longrightarrow \mathcal{R}_1(\mathcal{A}; \hat{H}) = 0. \tag{88}$$

The situation changes however already for $n = 2$. Indeed in this case, if $d_1 = 2$ we can get a rate of $\epsilon_1/2$, by using the following unitary operation:

$$\begin{aligned} |1_0 1_0\rangle &\longrightarrow |0 1_0\rangle, \\ |1_1 1_1\rangle &\longrightarrow |0 1_1\rangle, \\ |1_0 1_1\rangle &\longrightarrow |1_0 0\rangle, \\ |1_1 1_0\rangle &\longrightarrow |1_1 0\rangle, \end{aligned} \tag{89}$$

where we used $|1\rangle$, $|1'\rangle$ to represent the two orthogonal states $|\epsilon_{1,0}\rangle$ and $|\epsilon_{1,1}\rangle$ of level 1. More generally, for $d_1 > 1$ generic, we can use $n$ copies of the state we could extract the work $k\epsilon_1$ by promoting $k$ excited states into the ground level if the following conditions are satisfied

$$\#\mathrm{input}(n) \leqslant \#\mathrm{output}(n, k), \tag{90}$$

where $\#\mathrm{input}(n)$ and $\#\mathrm{output}(n, k)$ are the number of orthogonal configurations associated, respectively, with the $n$ copies of the input state and they transformed versions. The first number corresponds to the possible ways in which we form $n$-long strings with $d_1$ symbols, i.e., $\#\mathrm{input}(n) = d_1^n$, while the second corresponds to the possible ways in which we can form $n$-long strings using $d_1$ symbols under the constraint that $k$ elements are fixed equal to zero, i.e.,

$$\#\mathrm{output}(n, k) = \binom{n}{k} d_1^{n-k}.$$

Accordingly, Eq. (90) reduces to the constraint

$$C_{n,k}(d_1) := \binom{n}{k} - d_1^k \geqslant 0. \tag{91}$$

For each $n$, and $k$ fulfilling the above expression $k/n$ represents an achievable rate. Observe also that, for each fixed $n$, the maximum $k$ that is compatible with (91) represents the maximum rate attainable (indeed the only way we have to get energy from the system is to promote the excited state into the ground). Accordingly we can write

$$\mathcal{R}_n(\mathcal{A}; \hat{H}) = \epsilon_1 \max_k \{k/n : C_{n,k}(d_1) \geqslant 0\}, \tag{92}$$

$$\begin{aligned} \mathcal{R}(\mathcal{A}; \hat{H}) &= \epsilon_1 \lim_{n\to\infty} \max_k \{k/n : C_{n,k}(d_1) \geqslant 0\} \\ &= \epsilon_1 \max_{n,k} \{k/n : C_{n,k}(d_1) \geqslant 0\}. \end{aligned} \tag{93}$$

Recalling that for all $n$ and $k$ we have

$$\left(\frac{en}{k}\right)^k \geqslant \binom{n}{k} \geqslant \left(\frac{n}{k}\right)^k. \tag{94}$$

The lower bound implies that for $n, k$ such that $k/n \leqslant 1/d_1$ one has $C_{n,k}(d_1) \geqslant 0$; the upper bound instead can be used to verify that $k/n > e/d_1$ instead we always get $C_{n,k}(d_1) < 0$. Replacing this in the above expression yields the following bounds for $\mathcal{R}(\mathcal{A}; \hat{H})$:

$$e\epsilon_1/d_1 \geqslant \mathcal{R}(\mathcal{A}; \hat{H}) \geqslant \epsilon_1/d_1. \tag{95}$$

The above analysis can be easily extended to include also those configurations where the input states of the system do occupy all the full energy subspace $\mathcal{H}_1$ associated with the energy level $\epsilon_1$. In fact suppose that $\mathcal{A}$ covers only $\delta_1 < d_1$ of the vectors of $\mathcal{H}_1$, e.g.,

$$\mathcal{A} = \mathrm{Span}\{|\epsilon_{1,0}\rangle, \ldots, |\epsilon_{1,\delta_1-1}\rangle\} \subset \mathcal{H}_1, \quad \mathbb{S} = \{1\}. \tag{96}$$

Under this condition we can still use Eq. (90) to identify the work values which can be extracted deterministically: in this case however the left-hand-side term of such inequality assumes a smaller value [i.e., $\#\mathrm{input}(n) = \delta_1^n$], and (91) gets replaced by the weaker constraint

$$C_{n,k}(d_1, \delta_1) := \binom{n}{k} - d_1^k \left(\frac{\delta_1}{d_1}\right)^n \geqslant 0. \tag{97}$$

Inserting this into (92) and (93) leads to MDEW rates which are larger than or equal to the one obtained for $\delta_1 = d_1$, in agreement with the prediction of Lemma 3. For instance for $\delta_1 = 1$ and $d_1 \geqslant 2$ the inequality (97) can be always fulfilled with $k = n$ leading to $\mathcal{R}_n(\mathcal{A}; \hat{H}) = \epsilon_1$ which corresponds to the maximum work one can hope to extract from the system. More generally the new values of the rates are given by

$$\mathcal{R}_n(\mathcal{A}; \hat{H}) = \epsilon_1 \max_k \{k/n : C_{n,k}(d_1, \delta_1) \geqslant 0\}, \tag{98}$$

$$\begin{aligned} \mathcal{R}(\mathcal{A}; \hat{H}) &= \epsilon_1 \lim_{n\to\infty} \max_k \{k/n : C_{n,k}(d_1, \delta_1) \geqslant 0\} \\ &= \epsilon_1 \max_{n,k} \{k/n : C_{n,k}(d_1, \delta_1) \geqslant 0\}. \end{aligned} \tag{99}$$

### C. Free levels at higher energy

As established by Lemma 3 reducing the occupancies numbers $\overline{d}_i = \dim[\mathcal{A}_i]$ of the energy eigenspaces of the model tends to improve the MDEW of the model: this is a direct consequence of the fact that smaller values of the $\overline{d}_i$ corresponds to weaker constraints on the associated optimization problem. A similar effect arises when we increase the degeneracy of $\hat{H}$ while keeping the same occupation level of $\mathcal{A}$. For instance, in the example of Sec. VI B, setting $d_0 = d_1$, for $\mathcal{A}$ as in Eq. (87) will always allow for an optimal MDEW value rate of $\mathcal{R}_n(\mathcal{A}; \hat{H}) = \epsilon_1$. Strangely enough, the same phenomenon can also occur if we add extra levels to $\hat{H}$ with energy values that are *above* the one occupied by $\mathcal{A}$. To see this consider the case of a three-level model Hamiltonian $\hat{H}$ obtained by

adding an extra level $\epsilon_2 > \epsilon_1$ with degeneracy $d_2 \geqslant 1$ to the one presented in (86), i.e.,

$$\hat{H} = \epsilon_1 \sum_{j=0}^{d_1-1} |\epsilon_{1,j}\rangle\langle\epsilon_{1,j}| + \epsilon_2 \sum_{j=0}^{d_2-1} |\epsilon_{2,j}\rangle\langle\epsilon_{2,j}|. \tag{100}$$

while maintaining $\mathcal{A}$ as in (87), i.e., assigning zero occupation to both the ground level and the new one and assuming full occupancy for the intermediate level—see Fig. 4(d). Under these assumptions one would be tempted to conclude that the level $\epsilon_2$ plays no fundamental role in the energy extraction process: indeed promoting populations from $\epsilon_1$ to $\epsilon_2$ will cost an energy $\epsilon_2 - \epsilon_1$ which will contribute negatively on the overall budget. It turns out, however, that under certain conditions such a loss can be exploited to improve the MDEW efficiency above the one described in Eq. (92)—which in the context of the three-level model corresponds to the restricted set of TPM strategies where we can only move population from $\epsilon_1$ toward the ground state. To see this consider for instance the case where we have at disposal $n$ copies of the input state $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$. Given hence $k^\star$ the maximum $k$ that fulfils (91), from (92) we know that the strategies that convert states of $\epsilon_1$ into the ground can achieve at most the rate

$$\tilde{\mathcal{R}}_n(\mathcal{A}; \hat{H}) = \epsilon_1 k^\star / n \tag{101}$$

(notice that typically this will be smaller than $\epsilon_1$ since $k^\star < n$). Exploiting the presence of $\epsilon_2$ we can try to do better e.g., promoting $k^\star + 1$ states $\epsilon_1$ into the ground *and* one extra state $\epsilon_1$ into one of the levels $\epsilon_2$. Indeed assuming that such unitary exists we could gain a rate equal to

$$\begin{aligned}\mathcal{R}_n &= \frac{\epsilon_1(k^\star+1) - (\epsilon_2 - \epsilon_1)}{n} = \frac{\epsilon_1 k^\star + (2\epsilon_1 - \epsilon_2)}{n} \\ &= \tilde{\mathcal{R}}_n(\mathcal{A}; \hat{H}) + \frac{(2\epsilon_1 - \epsilon_2)}{n},\end{aligned} \tag{102}$$

which is greater than $\tilde{\mathcal{R}}_n(\mathcal{A}; \hat{H})$ whenever $2\epsilon_1 > \epsilon_2$. A sufficient condition for this to happens, is that there are sufficiently many output configurations with $k^\star + 1$ ground states, $n - (k^\star + 2)$ states $\epsilon_1$ and one state $\epsilon_2$, to accommodate the input configurations $\#\text{input}(n) = d_1^n$ of $\hat{\rho}^{\otimes n}$. Considering the degeneracy we have assumed for $\hat{H}$, the total number of the above output configurations can be explicitly computed: they are

$$\#\text{output}(n, k^\star + 1, 1) := \frac{n! d_1^{n-(k^\star+1)} d_2}{(n - k^\star - 2)!(k^\star + 1)!1!}. \tag{103}$$

Accordingly the possibility of reaching the rate (102) is determined by the inequality

$$d_2 \geqslant \left(\frac{(n - k^\star - 2)!(k^\star + 1)!}{n!}\right) d_1^{k^\star+1}. \tag{104}$$

As an example consider for instance what happens for $d_1 = 2$ and $n = 3$. Under this condition one notices that $k^\star = 1$, so that $k^\star/n = 1/3$. On the contrary the condition (104) becomes $d_2 \geqslant 4/3$: therefore it is sufficient to have $d_2 = 2$ to bring the rate from $\epsilon_1/3$ to $[\epsilon_1 + (2\epsilon_1 - \epsilon_2)]/3$. Notice that the presence of $d_2$ can be exploited to lead even more drastic improvements: for instance, for fixed $n$, one can try to promote $n - 1$ states to the ground paying the price of having a single state in $\epsilon_2$. Under this condition one could push the rate at

$$\mathcal{R}_n = \frac{(n-1)\epsilon_1 - (\epsilon_2 - \epsilon_1)}{n} = \epsilon_1 - \frac{\epsilon_2}{n}, \tag{105}$$

which for $n$ sufficiently large approximates the upper bound $\epsilon_1$ dictated by (64). The condition for this to happens is that $d_2$ is sufficiently large to ensure that the output configurations with $n - 1$ ground states and 1 state $\epsilon_2$ are larger than $\#\text{input}(n) = d_1^n$, i.e.,

$$n d_2 \geqslant d_1^n, \quad \Longrightarrow \quad d_2 \geqslant d_1^n / n. \tag{106}$$

## VII. RATIONAL SPECTRA

Building up from the examples analyzed in the previous section, here we focus on a special class of models for which one can explicitly prove that the asymptotic MDEW ratio is nonzero. Specifically we consider the case where the nonempty elements set $\mathbb{S}$ of the subspace $\mathcal{A}$ identifies energy levels of the Hamiltonian $\hat{H}$ that are proportional to integer numbers up to a common multiplicative factor $E$:

$$\forall\, i \in \mathbb{S} \quad \begin{cases} \hat{\Pi}_{\mathcal{A}_i} = \sum_{s=0}^{\overline{d}_i - 1} |\epsilon_{i,s}\rangle\langle\epsilon_{i,s}|, \hat{H}|\epsilon_{i,s}\rangle = \epsilon_i |\epsilon_{i,s}\rangle, \\ \forall\, i, s, i', s' : \langle\epsilon_{i,s}|\epsilon_{i',s'}\rangle = \delta_{ii'}\delta_{ss'}, \\ \exists\, m_i \in \mathbb{N} : \epsilon_i = E m_i, \end{cases} \tag{107}$$

where

$$\overline{d}_i := \dim[\mathcal{A}_i] \leqslant d_i \tag{108}$$

is the dimension of the $i$th energy block $\mathcal{A}_i$ of $\mathcal{A}$, and $\{|\epsilon_{i,s}\rangle\}_{s=1,\ldots,\overline{d}_i}$ an orthonormal basis for such space (of course such scenario includes as special instances the settings where the entire spectrum of $\hat{H}$—not just the part of it that it is filtered out in $\mathcal{A}$—fulfils the above requirement). Under the condition (107) we can prove that, as long as the ground state of the system is not populated, i.e., if $0 \notin \mathbb{S}$, the asymptotic MDEW ratio of the model is explicitly nonzero [of course if $0 \in \mathbb{S}$ then the MDEW ratio is always null due to Eq. (65)]. To do so we provide a lower bound for $\mathcal{R}(\mathcal{A}; \hat{H})$ which is explicitly not zero.

Assume hence $\mathbb{S}$ to be a collection of energy eigenvectors indexes which does not include the ground energy level and that contains at least two distinct elements [the case in which $\mathbb{S}$ has a unique element is already solved in Eq. (46)]. Define then $M_{\mathbb{S}}$ to be the least common multiplier of the integers $m_i$ associated with the populated part of the spectrum of $\hat{H}$, i.e.,

$$M_{\mathbb{S}} := \text{lcm}\{m_i : i \in \mathbb{S}\}, \tag{109}$$

and the quantities

$$K_i := \frac{M_{\mathbb{S}}}{m_i} + \overline{d}_i - 1, \tag{110}$$

$$K_{\mathbb{S}} := \sum_{i \in \mathbb{S}} \overline{d}_i (K_i - 1). \tag{111}$$

Notice that, by construction, the $m_i$ are all distinct integer numbers greater than or equal to 1, so we can conclude that $M_{\mathbb{S}} \geqslant 2$. Also it follows that the $K_i$ are all greater than or equal

to 1 and that

$$\frac{M_{\mathbb{S}}}{m_i} \neq \frac{M_{\mathbb{S}}}{m_j} \; \forall \, i \neq j \in \mathbb{S}. \tag{112}$$

Observe next that from Eq. (107) it follows that, for $n$ integer, the eigenvectors of $\hat{\omega}_{\mathcal{A}}^{\otimes n}(0)$ are provided by the tensor product states of the form

$$|\epsilon_{\vec{i},\vec{s}}\rangle := |\epsilon_{i_1,s_1}\rangle \otimes |\epsilon_{i_2,s_2}\rangle \otimes \cdots \otimes |\epsilon_{i_n,s_n}\rangle, \tag{113}$$

meaning that each eigenstate can be uniquely identify by a couple $(\vec{i},\vec{s}\,)$, with $\vec{i} := (i_1, i_2, \ldots, i_n) \in \mathbb{S}^n$ and $\vec{s} := (s_1, s_2, \ldots, s_n)$. Let $\mathbb{V}$ denote the set of allowed vectors:

$$\mathbb{V} := \{(\vec{i},\vec{s}\,) : \vec{i} \in \mathbb{S}^n \text{ and } \forall \; j, \; 0 \leqslant s_j < \overline{d}_i\}. \tag{114}$$

For each couple $(\vec{i},\vec{s}\,) \in \mathbb{V}$, we define $n_{j,u}(\vec{i},\vec{s}\,)$ as the number of copies of the terms $|\epsilon_{j,u}\rangle$ it contains: these quantities of course provide a partition of $n$, i.e., $\sum_{j\in\mathbb{S}} \sum_{u=0}^{\delta_j-1} n_{j,u}(\vec{i},\vec{s}\,) = n$. Observe also the following lemma:

*Lemma 4.* Given $n > K_{\mathbb{S}}$, for each $(\vec{i},\vec{s}\,) \in \mathbb{V}$ there exists $j^\star \in \mathbb{S}$ and $u^\star \in \{0, 1, \ldots, \delta_{j^\star} - 1\}$ such that $n_{j^\star,u^\star}(\vec{i},\vec{s}\,) \geqslant K_{j^\star}$.

*Proof.* Assume by contradiction that all $n_{j,u}(\vec{i},\vec{s}\,)$ are smaller than the corresponding $K_j$. Then we can write

$$\begin{aligned} n = \sum_{j\in\mathbb{S}} \sum_{u=0}^{\delta_j-1} n_{j,u}(\vec{i},\vec{s}) &\leqslant \sum_{j\in\mathbb{S}} \sum_{u=0}^{\delta_j-1} (K_j - 1) \\ &= \sum_{j\in\mathbb{S}} \delta_j (K_j - 1) = K_{\mathbb{S}}, \end{aligned} \tag{115}$$

which is impossible. ∎

As a consequence of the above result it follows that as long as $n \geqslant K_{\mathbb{S}} + 1$, then for each $(\vec{i},\vec{s}\,) \in \mathbb{V}$ we can assign the quantities

$$\begin{aligned} j_\star(\vec{i}) &:= \min\{j_\star \in \mathbb{S} : \exists \, u \text{ s.t. } n_{j_\star,u}(\vec{i},\vec{s}) \geqslant K_{j_\star}\}, \\ u_\star(\vec{i},\vec{s}) &:= \min\{u_\star : n_{j_\star(\vec{i}),u_\star}(\vec{i},\vec{s}) \geqslant K_{j_\star}\}, \\ K_\star(\vec{i}) &:= K_{j=j_\star(\vec{i})}. \end{aligned}$$

The set $\mathbb{V}$ can hence be divided into a collection of disjoint subsets which contain vectors $(\vec{i},\vec{s}\,)$ that have the same values of $j_\star(\vec{i}\,)$ and $u_\star(\vec{i},\vec{s}\,)$ [and hence the same $K_\star(\vec{i}\,)$], i.e.,

$$\begin{aligned} \mathbb{V} &:= \bigcup\nolimits_{a\in\mathbb{S}} \bigcup\nolimits_{0\leqslant b<\delta_a} \mathbb{V}_{a,b}, \\ \mathbb{V}_{a,b} &:= \{(\vec{i},\vec{s}\,) \in \mathbb{V} : j_\star(\vec{i}) = a, u_\star(\vec{i},\vec{s}) = b\}. \end{aligned} \tag{116}$$

By construction the couples of vectors included in $\mathbb{V}_{a,b}$ possess at least $K_a = \frac{M_{\mathbb{S}}}{m_a} + \delta_a - 1$ copies of the symbol $(a, b)$. For each $\mathbb{V}_{a,b}$ we can hence assign a new set of couples of $n$-dimensional vectors $\overline{\mathbb{V}}_{a,b}$ whose elements are obtained by taking the vectors of $\mathbb{V}_{a,b}$, and replacing $M_{\mathbb{S}}/m_a$ copies of the entry $(a, b)$ with (0,0). Since for each $(\vec{i},\vec{s}\,) \in \mathbb{V}_{a,b}$ there are at least

$$\binom{K_a}{M_{\mathbb{S}}/m_a} = \binom{M_{\mathbb{S}}/m_a + \delta_a - 1}{M_{\mathbb{S}}/m_a}$$

ways to do this, the size of $\overline{\mathbb{V}}_{a,b}$ must satisfy

$$|\overline{\mathbb{V}}_{a,b}| \geqslant \binom{M_{\mathbb{S}}/m_a + \delta_a - 1}{M_{\mathbb{S}}/m_a} |\mathbb{V}_{a,b}| \geqslant \delta_a |\mathbb{V}_{a,b}|, \tag{117}$$

meaning that for each $\mathbb{V}_{a,b}$ we can identify a subset $\tilde{\mathbb{V}}_{a,b} \subseteq \overline{\mathbb{V}}_{a,b}$ whose cardinality is exactly $|\tilde{\mathbb{V}}_{a,b}| = \delta_a |\mathbb{V}_{a,b}|$. Now let $\mathbb{V}_a := \bigcup_{b=0}^{\delta_a-1} \mathbb{V}_{a,b}$ and $\overline{\mathbb{V}}_a := \bigcup_{b=0}^{\delta_a-1} \overline{\mathbb{V}}_{a,b}$. The sets $\mathbb{V}_{a,b}$ are by construction disjoint, so

$$|\mathbb{V}_a| = \sum_{b=0}^{\delta_a-1} |\mathbb{V}_{a,b}|. \tag{118}$$

The size of the set $\overline{\mathbb{V}}_a$ satisfies instead the inequality

$$\begin{aligned} |\overline{\mathbb{V}}_a| = \left|\bigcup_{b=0}^{\delta_a-1} \overline{\mathbb{V}}_{a,b}\right| &\geqslant \left|\bigcup_{b=0}^{\delta_a-1} \tilde{\mathbb{V}}_{a,b}\right| \geqslant \max_b |\tilde{\mathbb{V}}_{a,b}| \\ &= \delta_a \max_b |\mathbb{V}_{a,b}| \geqslant \sum_{b=0}^{\delta_a-1} |\mathbb{V}_{a,b}| = |\mathbb{V}_a|. \end{aligned} \tag{119}$$

Recall that the elements of $\overline{\mathbb{V}}_{a,b}$ are characterized by $M_{\mathbb{S}}/K_a$ copies of the ground state. From Eq. (112) it follows that the sets $\overline{\mathbb{V}}_a$ do not overlap, i.e.,

$$\overline{\mathbb{V}}_a \cap \overline{\mathbb{V}}_{a'} = \varnothing \; \forall \; a \neq a' \in \mathbb{S}. \tag{120}$$

Accordingly we can identify a mapping $\mathcal{F}$ from $\mathbb{V} = \bigcup_{a\in\mathbb{S}} \mathbb{V}_a$ to $\bigcup_{a\in\mathbb{S}} \overline{\mathbb{V}}_a$ which for all $a$ sends $\mathbb{V}_a$ into a subset of $\overline{\mathbb{V}}_a$,

$$(\vec{i},\vec{s}\,) \in \mathbb{V}_a \mapsto \mathcal{F}(\vec{i},\vec{s}\,) \in \overline{\mathbb{V}}_a, \tag{121}$$

which is injective, i.e., such that $\mathcal{F}(\vec{i},\vec{s}\,) \neq \mathcal{F}(\vec{i}',\vec{s}\,')$ for all $(\vec{i},\vec{s}\,) \neq (\vec{i}',\vec{s}\,')$. From this we can now derive the following lower bound for the MDEW ratio,

$$\mathcal{R}(\mathcal{A};\hat{H}) \geqslant E \frac{M_{\mathbb{S}}}{K_{\mathbb{S}} + 1} > 0. \tag{122}$$

The proof relays on the observation that for $n \geqslant K_{\mathbb{S}} + 1$ there exists a unitary transformation $\hat{U}_{\mathcal{F}}^{(n)}$ which enables us to extract an amount $W = EM_{\mathbb{S}}$ of work deterministically. On the eigenvectors $|\epsilon_{\vec{i},\vec{s}}\rangle$ which form the support of $\hat{\omega}_{\mathcal{A}}^{\otimes n}(0)$ such unitary is simply the transformation which implement the mappings (121) defined above, i.e.,

$$\hat{U}_{\mathcal{F}}^{(n)} |\epsilon_{\vec{i},\vec{s}}\rangle = |\vec{\epsilon}_{\mathcal{F}(\vec{i},\vec{s})}\rangle \; \forall \; (\vec{i},\vec{s}\,) \in \mathbb{V}. \tag{123}$$

Due to the fact that for $(\vec{i},\vec{s}\,) \in \mathbb{V}_a$, the states $|\epsilon_{(\vec{i},\vec{s}\,)}\rangle$ and $|\vec{\epsilon}_{\mathcal{F}(\vec{i},\vec{s}\,)}\rangle$ only differs by the fact that in the latter $K_a$ copies of eigenvectors with energy eigenvalue $\epsilon_a$ are replaced with a ground-state vector, the associated energy gain for each one for all these transitions is equal to

$$W = K_a \epsilon_a = \frac{M_{\mathbb{S}}}{m_a} E m_a = EM_{\mathbb{S}}. \tag{124}$$

Accordingly for $\hat{\rho}$ with support $\mathcal{H}_{\mathbb{S}}$ we can write

$$\begin{aligned} &\left\langle W_{\hat{U}_{\mathcal{F}}^{(n)}}\left(\hat{\omega}_{\mathcal{A}}^{\otimes n}(0); \hat{H}^{(n)}\right)\right\rangle = EM_{\mathbb{S}}, \\ &\left\langle \Delta^2 W_{\hat{U}_{\mathcal{F}}^{(n)}}\left(\hat{\omega}_{\mathcal{A}}^{\otimes n}(0); \hat{H}^{(n)}\right)\right\rangle = 0, \\ &\qquad \Longrightarrow \mathcal{R}_n(\mathcal{A};\hat{H}) \geqslant \frac{EM_{\mathbb{S}}}{n}, \end{aligned} \tag{125}$$

The maximum of the above expression is achieved for $n = K_{\mathbb{S}} + 1$ which via (61) finally leads to (122).

In the special case in which the spectrum of the Hamiltonian is nondegenerate (i.e., $d_i = \overline{d}_i = 1 \Rightarrow K_i = M_{\mathbb{S}}/m_i$ for all $i$), using in (122) the definitions (109), (110), and (111), we can recast the lower bound (122) in a slightly weaker form which unveils a more straightforward and useful dependence on the energy levels $\epsilon_i$, i.e.,

$$\mathcal{R}(\mathcal{A};\hat{H}) \geqslant E\left(\sum_{i\in\mathbb{S}}\frac{1}{m_i}\right)^{-1} = \left(\sum_{i\in\mathbb{S}}\frac{1}{\epsilon_i}\right)^{-1}. \tag{126}$$

The difference between the bounds (126) and (122) becomes negligible when all the $m_i$ satisfy $m_i \gg d$.

### Finite-size behaviour

From the definition (62) and from (60) it follows that one always has

$$\mathcal{R}_{kn}(\mathcal{A};\hat{H}) \geqslant \mathcal{R}_n(\mathcal{A};\hat{H})\ \forall\, k, n \in \mathbb{N}. \tag{127}$$

Combining the above inequality with (125) we have

$$\mathcal{R}_n(\mathcal{A};\hat{H}) \geqslant \left\lfloor \frac{n}{K_{\mathbb{S}}+1}\right\rfloor \frac{EM_{\mathbb{S}}}{n}\ \forall\, n > K_{\mathbb{S}}, \tag{128}$$

which also implies that, for every $1/2 \leqslant c < 1$, we can write

$$\mathcal{R}_n(\mathcal{A};\hat{H}) \geqslant c\frac{EM_{\mathbb{S}}}{K_{\mathbb{S}}+1}\ \forall\, n > \frac{c}{1-c}K_{\mathbb{S}}. \tag{129}$$

As in the case of (126), for nondegenerate spectra this can also be cast in the weaker (yet simpler) form

$$\mathcal{R}_n(\mathcal{A};\hat{H}) \geqslant c\left(\sum_{i\in\mathbb{S}}\frac{1}{\epsilon_i}\right)^{-1}\ \forall\, n > \frac{c}{1-c}K_{\mathbb{S}}. \tag{130}$$

## VIII. GENERIC SPECTRA

In this section we are going to show that, by approximating the spectrum of a generic Hamiltonian to rational level, we can construct a work extraction protocol with bounded fluctuations (see Fig. 6).

*Lemma 5.* Let $\hat{H} = \sum_{j=0}^{M-1}\epsilon_j\hat{\Pi}_j$ and $\hat{H}' = \sum_{j=0}^{M-1}\epsilon'_j\hat{\Pi}_j$ be two Hamiltonians of form (1) characterized by the same degeneracies values and whose associated eigenvalues differ at most by a constant $\delta \geqslant 0$, i.e.,

$$|\epsilon'_j - \epsilon_j| < \delta\ \forall\, j \in \{0,\dots,M-1\}. \tag{131}$$

Suppose now that $\hat{H}'$ admits a unitary evolution $\hat{U}$ that permits to extract a deterministic work value $W' \geqslant 0$ for the input state $\hat{\rho}$, i.e., $P^{(\hat{H}')}_{\hat{\rho};\hat{U}}(w) = \delta(w - W')$. Then using $\hat{U}$ when the system Hamiltonian is $\hat{H}$, yields an average work extraction value

$$|\langle W_{\hat{U}}(\hat{\rho};\hat{H})\rangle - W'| \leqslant 2\delta, \tag{132}$$

and a probability distribution of the extracted work $P^{(\hat{H})}_{\hat{\rho};\hat{U}}(w)$, which is null whenever the distance of $w$ from $W'$ is larger than $2\delta$, i.e.,

$$P^{(\hat{H})}_{\hat{\rho};\hat{U}}(|w - W'| > 2\delta) := 1 - \int_{W'-2\delta}^{W'+2\delta} dw P^{(\hat{H})}_{\hat{\rho};\hat{U}}(w) = 0. \tag{133}$$

*Proof.* Invoking the condition (38) we know that $\hat{U}$ applied to $\hat{\rho}$, given $i \in \mathbb{S}[\hat{\rho}]$ the transition probabilities $P_{\hat{U}}(j|\hat{\rho}_i) = \mathrm{Tr}[\hat{\Pi}_j\hat{U}\hat{\rho}_i\hat{U}^\dagger]$ is equal to one for $j$ such that $\epsilon'_i - \epsilon'_j = W'$, and zero otherwise. Observe hence that according to (131), when working with the Hamiltonian $\hat{H}$ the same mapping will assign probability equal to one to energy jumps $\epsilon_i \mapsto \epsilon_j$ which fulfils the inequality $|\epsilon_i - \epsilon_j - W'| \leqslant 2\delta$, and zero otherwise:

$$P_{\hat{U}}(j|\hat{\rho}_i) = \begin{cases} 1 & \text{for } |\epsilon_j - \epsilon_i - W'| \leqslant 2\delta, \\ 0 & \text{otherwise.} \end{cases} \tag{134}$$

The thesis finally follows by replacing the above identity in Eqs. (32) and (30). ■

*Remark.* Observe that the above result can also be generalized to situations in which $\hat{H}$ and $\hat{H}'$ commute by have different degeneracies. In particular consider the case where $\hat{H}'$ is nondegenerate with eigenvalues $\epsilon'_0,\dots,\epsilon'_{d-1}$, while $\hat{H}$ has only $M < d$ distinct eigenvalues $\epsilon_0,\dots,\epsilon_{M-1}$. Assume now that we can organize the element of the spectrum of $\hat{H}'$ into $M$ groups $\mathbb{G}'_0, \mathbb{G}'_1, \dots, \mathbb{G}'_{M-1}$ such that

$$|\epsilon' - \epsilon_j| < \delta\ \forall\, j \in \{0,\dots,M-1\}\ \forall\, \epsilon' \in \mathbb{G}'_j. \tag{135}$$

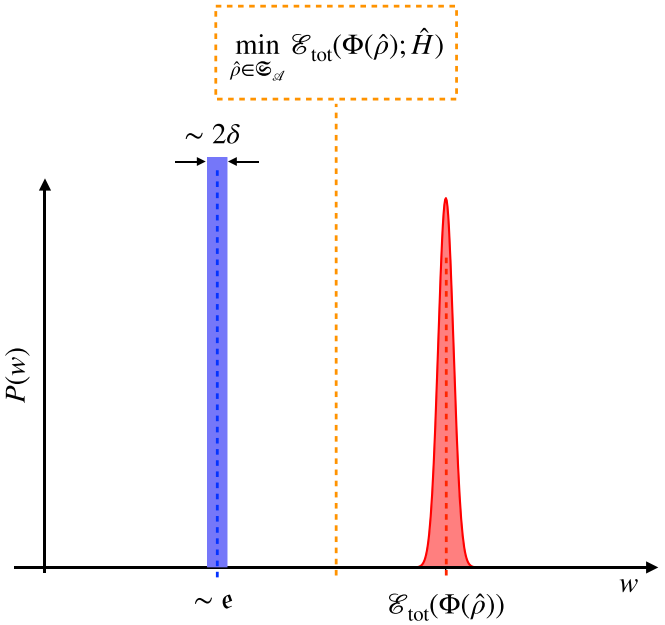


FIG. 6. Comparison between the bounded fluctuation protocol presented here and the collective protocol of Ref. [31]. The typicality-based protocol of Ref. [31] can extract the maximal energy $\mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho}))$, with exponentially suppressed fluctuations. In contrast, the protocol discussed in this section can extract an energy $\approx\mathfrak{e} < \mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho}))$, but with the guarantee that the work fluctuation never exceeds $4\delta$. Protocols with bounded fluctuation may exist for higher value of the mean extracted work, up until the upper bound (67), which is always smaller than or equal to $\mathcal{E}_{\mathrm{tot}}(\Phi(\hat{\rho}))$ [with the equality holding only in the case in which $\hat{\rho} = \hat{\omega}_{\mathcal{A}}(\beta^\star)$].

Then following the same derivation given in Lemma 5 can be used to show that if $P^{(\hat{H}')}_{\hat{\rho};\hat{U}}(w) = \delta(w - W')$ for some $\hat{U}$ and $W'$, then Eqs. (132) and (133) still applies.

*Lemma 6.* Given a generic Hamiltonian $\hat{H} = \sum_{i=0}^{M-1} \epsilon_i \hat{\Pi}_i$ and $\mathcal{A} := \bigoplus_{i=0}^{M-1} \mathcal{A}_i$ a direct sum of subsets of its energy eigenspaces, let

$$\mathfrak{e} := \left( \sum_{i \in \mathbb{S}} \frac{\overline{d}_i}{\epsilon_i} \right)^{-1}, \tag{136}$$

with $\mathbb{S}$ the nonempty elements set (13) of $\mathcal{A}$ and with $\overline{d}_i = \dim[\mathcal{A}_i]$ the dimension of its $i$th energy block. Then for each $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$ and $c \in [0, 1[$, we can identify a positive constant $A$ with the property that, for each $\delta > 0$ sufficiently small, given $n > A\delta^{-|\mathbb{S}|+1}$ copies of $\hat{\rho}$, we can find a TPM protocol acting on $\hat{\rho}^{\otimes n}$ such that

$$W := \langle W_{\hat{U}}(\hat{\rho}^{\otimes n}; .\hat{H}^{(n)}/n) \rangle \geqslant c\mathfrak{e} - 2\delta, \tag{137}$$

$$P^{(\hat{H}^{(n)}/n)}_{\hat{\rho}^{\otimes n};\hat{U}}(|w - W| > 4\delta) = 0. \tag{138}$$

*Proof.* Define $\{|\epsilon_{i,j}\rangle : j = 0, \ldots, d_i - 1\}$ as the orthonormal basis of the energy subspace $\mathcal{H}_i$ of $\hat{H}$ constructed by taking as the first $\overline{d}_i$ elements those which define the orthonormal basis of $\mathcal{A}_i$ introduced in Eq. (107). For $\delta > 0$ and $i \in \{0, \ldots, M-1\}$ we now introduce the integer constants

$$m_{i,j} := \left\lfloor \frac{\epsilon_i}{\delta/d^\star} \right\rfloor + j + 1, \quad s \in \{0, \ldots, d_i - 1\}, \tag{139}$$

where $\epsilon_i$ are the eigenvalues of $\hat{H}$ and $d^\star = \max_j d_j$ is its maximum degeneracy. We hence define the Hamiltonian

$$\hat{H}' := \sum_{i=0}^{M-1} \sum_{j=0}^{d_i - 1} \epsilon'_{i,j} |\epsilon_{i,j}\rangle\langle\epsilon_{i,j}|, \tag{140}$$

with eigenvalues

$$\epsilon'_{i,j} := m_{i,j} \frac{\delta}{d^\star}. \tag{141}$$

which by construction commute with $\hat{H}$ and $\mathcal{A}$. Notice also that we have

$$\epsilon_i + \delta \geqslant \epsilon'_{i,j} \geqslant \epsilon_i, \tag{142}$$

for all $i \in \{0, \ldots, M-2\}$ and for all $j \in \{0, \ldots, d_i - 1\}$. Furthermore, if we take

$$\delta < \min_{i \in \{0,\ldots,M-2\}} (\epsilon_{i+1} - \epsilon_i), \tag{143}$$

from (142) ensures that $\epsilon_{i+1} > \epsilon_i + \delta > \epsilon'_{i,j}$ implying that the spectrum of $\hat{H}'$ is nondegenerate. Notice also that the subset $\mathcal{A}$ can be expressed as a direct sum of energy subspaces of $\hat{H}'$ with a nonempty index subset $\mathbb{S}'$ identified by the couples $\{(i,j) : i \in \mathbb{S}, j \in \{0, \ldots, \overline{d}_i\}\}$. Notice also that the Hamiltonian $\hat{H}'$ falls therefore under the hypotheses of Sec. VII, and we can invoke (130) to deduce that, for each $n > \frac{c}{1-c} K_{\mathbb{S}'}$, one has

$$\mathcal{R}_n(\mathcal{A}; \hat{H}') \geqslant c \left( \sum_{(i,j) \in \mathbb{S}'} \frac{1}{\epsilon'_{i,j}} \right)^{-1} \geqslant c \left( \sum_{(i,j) \in \mathbb{S}'} \frac{1}{\epsilon_i} \right)^{-1} = c\mathfrak{e}, \tag{144}$$

where in the second inequality we use the leftmost part of (142). This means that there exists a unitary $\hat{U}$ such that it allows us to deterministically extract a work value larger than or equal to $c\mathfrak{e}$ from $n > \frac{c}{1-c} K_{\mathbb{S}'}$ copies of a generic density matrix $\hat{\rho} \in \mathfrak{S}_{\mathcal{A}}$, i.e.,

$$W' := \langle W_{\hat{U}}(\hat{\rho}^{\otimes n}; \hat{H'}^{(n)}/n) \rangle \geqslant c\mathfrak{e}, \quad \langle \Delta^2 W_{\hat{U}}(\hat{\rho}^{\otimes n}; \hat{H'}^{(n)}/n) \rangle = 0. \tag{145}$$

Observe next that the $n$-copy Hamiltonians $\hat{H}^{(n)}/n$ and $\hat{H}'^{(n)}/n$ have eigenvalues

$$\epsilon_{\vec{i}}/n := \sum_{s=1}^{n} \frac{\epsilon_{i_s}}{n}, \quad \vec{i} \in \{0, \ldots, M-1\}^n,$$

$$\epsilon'_{\vec{i},\vec{j}}/n := \sum_{s=1}^{n} \frac{\epsilon'_{i_s,j_s}}{n}, \quad \begin{cases} \vec{i} \in \{0, \ldots, M-1\}^n, \\ \vec{j} \in \mathbb{D}_{\vec{i}}, \end{cases}$$

with $\mathbb{D}_{\vec{i}}$ defined implicitly by (140), which satisfy the condition (135). Indeed identifying $\mathbb{G}'_{\vec{i}}$ as the set formed by the elements $\epsilon'_{\vec{i},\vec{j}}/n$ with $\vec{j} \in \mathbb{D}_{\vec{i}}$, from Eq. (142) we get:

$$\left| \frac{\epsilon'_{\vec{i},\vec{j}}}{n} - \frac{\epsilon_{\vec{i}}}{n} \right| \leqslant \frac{1}{n} \sum_{s=1}^{n} \left| \epsilon'_{i_s,j_s} - \epsilon_{i_s} \right| \leqslant \frac{1}{n} \sum_{s=1}^{n} \delta = \delta. \tag{146}$$

Applying the identity (132) of Lemma 5 to the pair of Hamiltonians $\hat{H}^{(n)}$ and $\hat{H}'^{(n)}$ ensures therefore that the same unitary $\hat{U}$ that realizes (145), also fulfils

$$|W - W'| \leqslant 2\delta, \tag{147}$$

which implies (137). Similarly from (133) of Lemma 5 we get

$$0 = P^{(\hat{H}^{(n)}/n)}_{\hat{\rho}^{\otimes n};\hat{U}}(|w - W'| > 2\delta) = P^{(\hat{H}^{(n)}/n)}_{\hat{\rho}^{\otimes n};\hat{U}}(|(w - W) + (W' - W)| > 2\delta),$$

which together with (147) leads to (138). To complete the proof, we observe that the constant $K_{\mathbb{S}'}$ can be bounded with

$$K_{\mathbb{S}'} < \sum_{i,j} \frac{M_{\mathbb{S}'}}{m_{i,j}} < \prod_{i,j} m_{i,j} \sum_{i,j} \frac{1}{m_{i,j}} \tag{148}$$

$$< |\mathbb{S}'| (\max_{i,j} m_{i,j})^{|\mathbb{S}'|-1} \leqslant |\mathbb{S}'| \left( \frac{d^\star \epsilon_{d-1}}{\delta} + d^\star \right)^{|\mathbb{S}'|-1} \leqslant d^\star |\mathbb{S}| \left( \frac{d^\star \epsilon_{d-1}}{\delta} + d^\star \right)^{d^\star|\mathbb{S}|-1} = d^\star |\mathbb{S}| (d^\star \epsilon_{d-1} + d^\star \delta)^{d^\star|\mathbb{S}|-1} \delta^{-d^\star|\mathbb{S}|+1}, \tag{149}$$

where in the third line we invoke the monotonicity under $|\mathbb{S}'|$ and the inequality $|\mathbb{S}'| \leqslant d^\star |\mathbb{S}|$. To identify the constant $A$

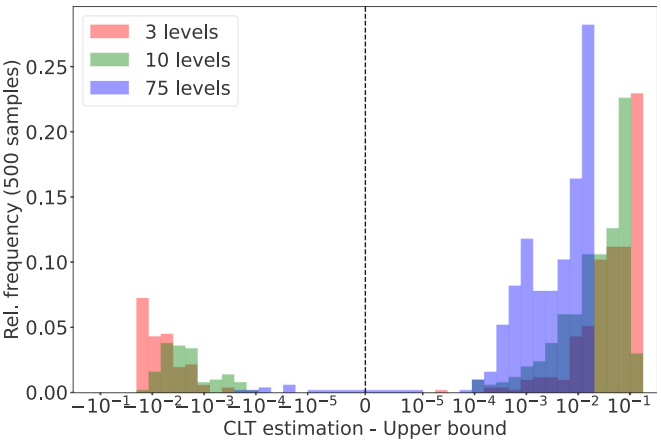


FIG. 7. Empirical distribution of the difference between the formula (163) and the rigorous upper bound (67), for 500 randomly chosen energy spectra of dimension $d = 3$, $d = 10$, and $d = 75$. The gaps between subsequent energy levels in the random Hamiltonians are independent samples from the uniform distribution; and the subspace $\mathcal{A}$ is the one generated by all the energy levels except for the ground state.

finally observe that for sufficiently small $\delta$ we can also write

$$K_{\mathbb{S}'} < d^\star|\mathbb{S}|(d^\star\epsilon_{d-1}+1)^{d^\star|\mathbb{S}|-1}\delta^{-d^\star|\mathbb{S}|+1}, \tag{150}$$

which gives the thesis by taking

$$A = \frac{c}{1-c}d^\star|\mathbb{S}|(d^\star\epsilon_{d-1}+1)^{d^\star|\mathbb{S}|-1}. \tag{151}$$

■

## IX. A SEMIHEURISTIC ESTIMATION BASED ON THE CENTRAL LIMIT THEOREM

In this section we want to derive a closed formula expression that, although not exact, does often closely approximate the asymptotic MDEW ratio $\mathcal{R}(\mathcal{A}, \hat{H})$. The idea is to use the central limit theorem to approximately count the number of energy levels of a given energy within the subspace $\mathcal{A}^{\otimes n}$ and the complete Hilbert space $\mathcal{H}^{\otimes n}$. We are not able to derive rigorous bound for the validity of this approximation. However, we find empirically that the difference between the estimation given by the formula (163), that we derive here, and the upper bound (67), for a randomly chosen Hamiltonian seems to approach zero as the size of the Hilbert space $\mathcal{H}$ increases (see Figs. 7 and 8).

Let $\hat{H}$ be a Hamiltonian satisfying the hypotheses of Sec. VII. We define the integer quantities $\mathfrak{n}_0(x,n)$ and $\mathfrak{n}_+(x,n)$ as the number of energy levels with energy equal to $nx$ in, respectively, $\hat{H}^{(n)}$ and $\mathcal{A}^{\otimes n}$. Explicitly,

$$\mathfrak{n}_0(x,n) := \#\left\{\vec{i}\in[0,d-1]^n : \sum_{s=1}^n \epsilon_{i_s} = nx\right\}, \tag{152}$$

$$\mathfrak{n}_+(x,n) := \#\left\{\vec{i}\in\mathbb{S}^n : \sum_{s=1}^n \epsilon_{i_s} = nx\right\}, \tag{153}$$

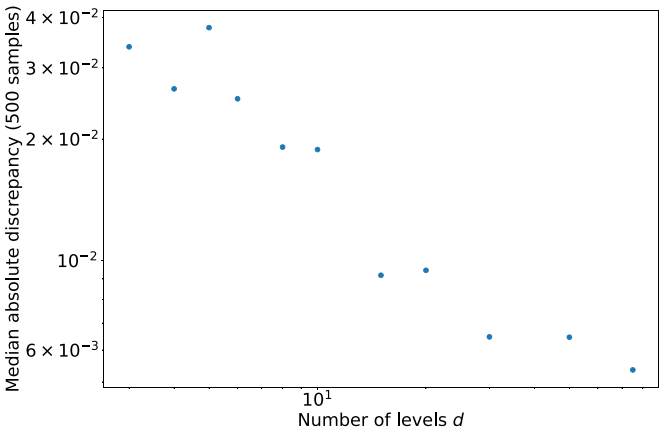


FIG. 8. Median absolute discrepancies between the CLT-based estimation (163) and the upper bound (67), for samples of 500 random energy spectra drawn from the same distribution as the one used in Fig. 7.

where we are using the symbol # to denote the cardinality of a set. Then the evaluation of (61) can be reformulate as

$$\mathcal{R}_n(\mathcal{A},\hat{H}) = \max\{\delta : \forall\, x\mathfrak{n}_+(x,n) \leqslant \mathfrak{n}_0(x-\delta,n)\}. \tag{154}$$

We observe incidentally that $\mathfrak{n}_0(x,n)$ and $\mathfrak{n}_+(x,n)$ can be expressed as polynomial coefficients in the expansions

$$\left(\sum_{j=0}^{d-1} z^{\epsilon_j}\right)^n = \sum_{i=0}^{nd-1}\mathfrak{n}_0\left(\frac{i}{n},n\right)z^i,$$
$$\left(\sum_{j\in\mathbb{S}} z^{\epsilon_j}\right)^n = \sum_{i=0}^{nd-1}\mathfrak{n}_+\left(\frac{i}{n},n\right)z^i, \tag{155}$$

which allow for their efficient numerical computation. Let us hence define

$$\mu_0 := \frac{1}{d}\sum_{i=0}^{d-1}\epsilon_d, \quad \sigma_0^2 := \frac{1}{d}\sum_{i=0}^{d-1}\epsilon_i^2 - \mu_0^2,$$
$$\mu_+ := \frac{1}{|\mathbb{S}|}\sum_{i\in\mathbb{S}}\epsilon_d, \quad \sigma_+^2 := \frac{1}{|\mathbb{S}|}\sum_{i\in\mathbb{S}}\epsilon_i^2 - \mu_+^2. \tag{156}$$

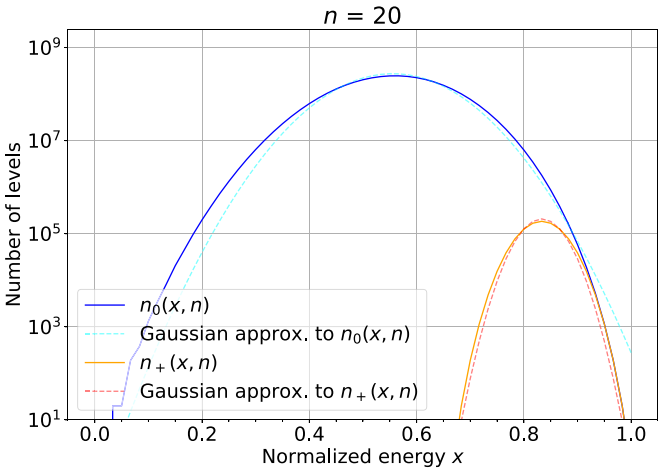


FIG. 9. The distribution of energy levels (152) and (153), compared with their Gaussian estimations (157) and (158), for $n = 20$ copies of the three-level Hamiltonian $\hat{H} = \frac{2}{3}|1\rangle\langle 1| + |2\rangle\langle 2|$, when $\mathcal{A} = \mathrm{Span}\{|1\rangle, |2\rangle\}$.

For large enough $n$, the central limit theorem allows us to approximate the energy level densities as

$$\mathfrak{n}_0(x,n) \simeq \frac{d^n}{n}\frac{\sqrt{n}}{\sqrt{2\pi\sigma_0^2}}\exp\left[-\frac{n(x-\mu_0)^2}{2\sigma_0^2}\right], \tag{157}$$

$$\mathfrak{n}_+(x,n) \simeq \frac{|\mathbb{S}|^n}{n}\frac{\sqrt{n}}{\sqrt{2\pi\sigma_+^2}}\exp\left[-\frac{n(x-\mu_+)^2}{2\sigma_+^2}\right], \tag{158}$$

see Fig. 9 for an illustrative example. Exploiting Eqs. (157) and (158), the condition $\forall\ x\mathfrak{n}_+(x,n) \leqslant \mathfrak{n}_0(x-\delta,n)$ from (154) becomes

$$\frac{|\mathbb{S}|^n}{\sqrt{2\pi\sigma_+^2}}\exp\left[-\frac{n(x-\mu_+)^2}{2\sigma_+^2}\right] \leqslant \frac{d}{\sqrt{2\pi\sigma_0^2}}\exp\left[-\frac{n(x-\delta-\mu_0)^2}{2\sigma_0^2}\right], \quad \forall x \tag{159}$$

which with some simple algebraic manipulation can be cast in the form

$$x^2\left(\frac{1}{2\sigma_+^2}-\frac{1}{2\sigma_0^2}\right)-2x\left(\frac{\mu_+}{2\sigma_+^2}-\frac{\mu_0+\delta}{2\sigma_0^2}\right)+\left(\frac{\mu_+^2}{2\sigma_+^2}-\frac{(\mu_0+\delta)^2}{2\sigma_0^2}+\ln\frac{d}{|\mathbb{S}|}+\frac{1}{n}\ln\frac{\sigma_+}{\sigma_0}\right)\geqslant 0\ \forall\, x. \tag{160}$$

The discriminant of the above quadratic form is equal to

$$\Delta=\frac{(\mu_0-\mu_++\delta)^2}{\sigma_+^2\sigma_0^2}-\left(\ln\frac{d}{|\mathbb{S}|}+\frac{1}{n}\ln\frac{\sigma_+}{\sigma_0}\right)\frac{2\sigma_0^2-2\sigma_+^2}{\sigma_+^2\sigma_0^2}. \tag{161}$$

In order for the condition (160) to hold true, we need that $\sigma_0^2>\sigma_+^2$ and that $\Delta\leqslant 0$. Solving (161) for $\delta$, we find that the requirement $\Delta\leqslant 0$ is equivalent to

$$\delta\leqslant\mu_+-\mu_0+\sqrt{2\left(\sigma_0^2-\sigma_+^2\right)}\sqrt{\left(\ln\frac{d}{|\mathbb{S}|}+\frac{1}{n}\ln\frac{\sigma_+}{\sigma_0}\right)}, \tag{162}$$

which, in the $n\to\infty$ limit, leads to the estimation

$$\mathcal{R}(\mathcal{A},\hat{H})\simeq\mu_+-\mu_0+\sqrt{2\left(\sigma_0^2-\sigma_+^2\right)}\sqrt{\ln\frac{d}{|\mathbb{S}|}}. \tag{163}$$

## X. CONCLUSIONS

We have derived upper and lower bounds on the asymptotic maximal deterministic work extraction (MDEW) rate, which quantifies the maximal work that can be extracted from a quantum system, without fluctuations, in the limit of infinite copies of the system. We found a lower bound that is strictly greater than zero for any Hamiltonian with rational spectra, meaning that, given enough copies of the system, deterministic work extraction is always possible for such Hamiltonians. Numerical evidence suggests that the actual MDEW rate may coincide with, or be very close to, the upper bound we derived, but we were not able to prove this definitively.

For Hamiltonians with incommensurable energy levels, although strictly deterministic work extraction may not be achievable, we have shown that with enough copies it is possible to bound the fluctuations in the extracted work to an arbitrarily small tolerance. Our protocols for bounded-fluctuation work extraction may find applications in quantum heat engines or batteries where a reliable, stable work output is critical.

More broadly, the scheme that we have introduced for manipulating ensembles of noninteracting copies of a quantum system may have implications for bounding fluctuations of other quantities through global quantum operations on multiple copies. This could aid in the design of stable quantum devices functioning in the finite-copies regime. An open question is whether allowing interactions between copies can enhance deterministic work extraction yields beyond the independent-copy bounds we have derived.

## ACKNOWLEDGMENTS

We acknowledge financial support by MUR (Ministero dell'Istruzione, dell'Università e della Ricerca) through the PNRR MUR project PE0000023-NQSTI.

## APPENDIX A: OPTIMALITY OF EQ. (68)

Here we show that, at least for those cases where the restriction of $\hat{H}$ over the subspace $\mathcal{A}$ is not degenerate, then

$$\min_{\Phi(\hat{\rho})\in\mathfrak{S}_{\mathcal{A}}}\mathcal{E}_{\rm tot}(\Phi(\hat{\rho});\hat{H})=\min_{\beta>0}\mathcal{E}_{\rm tot}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H}). \tag{A1}$$

To see this recall first that the total ergotropy of a generic state $\hat{\rho}$ corresponds to [23,39]

$$\mathcal{E}_{\rm tot}(\hat{\rho};\hat{H})={\rm Tr}[\hat{\rho}\hat{H}]-{\rm Tr}[\hat{\tau}_{\beta(\hat{\rho})}\hat{H}], \tag{A2}$$

with $\hat{\tau}_{\beta(\hat{\rho})}$ being the thermal Gibbs state whose inverse temperature $\beta(\hat{\rho})$ is fixed in order to ensure that the von Neumann entropy of such a state equals that of $\hat{\rho}$, i.e.,

$$S(\hat{\tau}_{\beta(\hat{\rho})})=S(\hat{\rho}). \tag{A3}$$

Observe next that if $\hat{H}$ is not degenerate, the entropy of the Gibbs-like density matrices $\hat{\omega}_{\mathcal{A}}(\beta)$ span continuously from 0 (for $\beta\to\infty$) to $\ln{\rm Tr}[\hat{\Pi}_{\mathcal{A}}]$ (for $\beta\to 0$) which is the maximum value allowed for states with support in $\mathcal{A}$. Given hence $\Phi(\hat{\rho})$ a diagonal ensemble in $\mathfrak{S}_{\mathcal{A}}$, we can always find $\beta^\star$ such that the Gibbs-like density matrix $\hat{\omega}_{\mathcal{A}}(\beta^\star)$ has entropy equal to that of $\Phi(\hat{\rho})$. In such a case $\hat{\tau}_{\beta(\Phi(\hat{\rho}))}$ and $\hat{\tau}_{\beta(\hat{\omega}_{\mathcal{A}}(\beta^\star))}$ will match, allowing us to write

$$\begin{aligned}\mathcal{E}_{\rm tot}(\Phi(\hat{\rho});\hat{H})&={\rm Tr}[\Phi(\hat{\rho})\hat{H}]-{\rm Tr}[\hat{\tau}_{\beta(\hat{\rho})}\hat{H}]\\&={\rm Tr}[\Phi(\hat{\rho})\hat{H}]-{\rm Tr}[\hat{\tau}_{\beta(\hat{\omega}_{\mathcal{A}}(\beta^\star))}\hat{H}]\\&\geqslant{\rm Tr}[\hat{\omega}_{\mathcal{A}}(\beta^\star)\hat{H}]-{\rm Tr}[\hat{\tau}_{\beta(\hat{\omega}_{\mathcal{A}}(\beta^\star))}\hat{H}]\\&=\mathcal{E}_{\rm tot}(\hat{\omega}_{\mathcal{A}}(\beta^\star);\hat{H}),\end{aligned} \tag{A4}$$

where the last inequality follows from the fact that $\hat{\omega}_{\mathcal{A}}(\beta^\star)$ is the state with the minimal energy among those which have the same support and the same entropy, so that

$${\rm Tr}[\Phi(\hat{\rho})\hat{H}]\geqslant{\rm Tr}[\hat{\omega}_{\mathcal{A}}(\beta^\star)\hat{H}]. \tag{A5}$$

To see this last fact observer that for $\beta$ arbitrary, invoking the Klein inequality we can write

$$\begin{aligned}0 \leqslant S(\Phi(\hat{\rho})\|\hat{\omega}_{\mathcal{A}}(\beta)) &= -S(\Phi(\hat{\rho})) - \mathrm{Tr}[\Phi(\hat{\rho})\ln\hat{\omega}_{\mathcal{A}}(\beta)]\\ &= -S(\Phi(\hat{\rho})) + \beta\mathrm{Tr}[\Phi(\hat{\rho})\hat{H}] + \ln Z_{\mathcal{A}}(\beta)\\ &= -S(\Phi(\hat{\rho})) + \beta\mathrm{Tr}[\hat{\omega}_{\mathcal{A}}(\beta)\hat{H}] + \ln Z_{\mathcal{A}}(\beta)\\ &\quad + \beta(\mathrm{Tr}[\Phi(\hat{\rho})\hat{H}] - \mathrm{Tr}[\hat{\omega}_{\mathcal{A}}(\beta)\hat{H}])\\ &= -S(\Phi(\hat{\rho})) + S(\hat{\omega}_{\mathcal{A}}(\beta)) + \beta(\mathrm{Tr}[\Phi(\hat{\rho})\hat{H}]\\ &\quad - \mathrm{Tr}[\hat{\omega}_{\mathcal{A}}(\beta)\hat{H}]),\end{aligned} \tag{A6}$$

where in the second identity we used the fact that $\Phi(\hat{\rho}) = \Phi(\hat{\rho})\hat{\Pi}_{\mathcal{A}}$ to write

$$\begin{aligned}\mathrm{Tr}[\Phi(\hat{\rho})\ln\hat{\omega}_{\mathcal{A}}(\beta)] &= \mathrm{Tr}\left[\Phi(\hat{\rho})\hat{\Pi}_{\mathcal{A}}\ln\left(\frac{\sum_{i\in\mathbb{S}}\hat{\Pi}_{\mathcal{A}_i}e^{-\beta\epsilon_i}}{Z_{\mathcal{A}}(\beta)}\right)\right]\\ &= \beta\mathrm{Tr}\left[\Phi(\hat{\rho})\hat{\Pi}_{\mathcal{A}}\sum_{i\in\mathbb{S}}\hat{\Pi}_{\mathcal{A}_i}\epsilon_i\right] + \ln Z_{\mathcal{A}}(\beta)\\ &= \beta\mathrm{Tr}[\Phi(\hat{\rho})\hat{H}] + \ln Z_{\mathcal{A}}(\beta).\end{aligned} \tag{A7}$$

The inequality (A5) finally follows from (A6) by simply reorganizing the various terms and taking $\beta = \beta^\star$. Since (A4) applies to all density matrices $\Phi(\hat{\rho}) \in \mathfrak{S}_{\mathcal{A}}$ we conclude that the minimization (67) can be replaced with (68) leading to (A1).

## APPENDIX B: PROOF OF EQ. (69)

We start by defining the real functions

$$\mathfrak{E}_0(\beta) := \mathrm{Tr}[\hat{\tau}_\beta\hat{H}], \quad \mathfrak{E}_{\mathcal{A}}(\beta) := \mathrm{Tr}[\hat{\omega}_{\mathcal{A}}(\beta)\hat{H}], \tag{B1}$$

$$\mathcal{S}_0(\beta) := S(\hat{\tau}_\beta), \quad \mathcal{S}_{\mathcal{A}}(\beta) := S(\omega_{\mathcal{A}}(\beta)), \tag{B2}$$

$$Z_0(\beta) := \mathrm{Tr}[e^{\beta\hat{H}}], \quad Z_{\mathcal{A}}(\beta) := \mathrm{Tr}[\hat{\Pi}_{\mathcal{A}}e^{\beta\hat{H}}], \tag{B3}$$

with $\tau_\beta$ and $\hat{\omega}_{\mathcal{A}}(\beta)$ as in Eqs. (69) and (16), respectively. The above functions satisfy the relationships

$$\mathcal{S}_0(\beta) = \beta\mathfrak{E}_0(\beta) + \ln Z_0(\beta), \tag{B4}$$

$$\mathcal{S}_{\mathcal{A}}(\beta) = \beta\mathfrak{E}_{\mathcal{A}}(\beta) + \ln Z_{\mathcal{A}}(\beta). \tag{B5}$$

By deriving (B4) with respect to the variable $\beta$ we have the following relations:

$$\frac{\mathrm{d}\mathcal{S}_0}{\mathrm{d}\beta} = \beta\frac{\mathrm{d}\mathfrak{E}_0}{\mathrm{d}\beta}, \quad \frac{\mathrm{d}\mathcal{S}_{\mathcal{A}}}{\mathrm{d}\beta} = \beta\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta}. \tag{B6}$$

For fixed $\beta$ define now $\beta^\star$ the inverse temperature such that $S(\hat{\omega}_{\mathcal{A}}(\beta)) = S(\hat{\tau}_{\beta^\star})$, i.e.,

$$\beta^\star(\beta) = \mathcal{S}_0^{-1}(S_{\mathcal{A}}(\beta)). \tag{B7}$$

Deriving (B7) and then applying (B6) we have that

$$\frac{\mathrm{d}\beta^\star}{\mathrm{d}\beta} = \frac{\mathrm{d}\beta^\star}{\mathrm{d}S_{\mathcal{A}}}\frac{\mathrm{d}S_{\mathcal{A}}}{\mathrm{d}\beta} = \frac{\mathrm{d}\beta^\star}{\mathrm{d}S_0}\frac{\mathrm{d}S_{\mathcal{A}}}{\mathrm{d}\beta} = \frac{\beta}{\beta^\star}\frac{\mathrm{d}\beta^\star}{\mathrm{d}\mathfrak{E}_0}\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta}. \tag{B8}$$

Notice next that, using the expression (A2) for the total ergotropy, the right-hand-side of the upper bound (68) can be expressed as

$$\mathcal{E}_{\mathrm{tot}}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H}) = \mathfrak{E}_{\mathcal{A}}(\beta) - \mathfrak{E}_0(\beta^\star(\beta)). \tag{B9}$$

Deriving (B9) and then using the chain rule and (B8) we obtain

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}\beta}\mathcal{E}_{\mathrm{tot}}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H})\\ &= \frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} - \frac{\mathrm{d}}{\mathrm{d}\beta}\mathfrak{E}_0(\beta^\star(\beta)) = \frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} - \frac{\mathrm{d}\mathfrak{E}_0}{\mathrm{d}\beta^\star}\frac{\mathrm{d}\beta^\star}{\mathrm{d}\beta}\\ &= \frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} - \frac{\beta}{\beta^\star}\frac{\mathrm{d}\mathfrak{E}_0}{\mathrm{d}\beta^\star}\frac{\mathrm{d}\beta^\star}{\mathrm{d}\mathfrak{E}_0}\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} = \left(1 - \frac{\beta}{\beta^\star}\right)\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta}.\end{aligned}$$

Every stationary point of $\mathcal{E}_{\mathrm{tot}}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H})$ must satisfy $\frac{\mathrm{d}}{\mathrm{d}\beta}\mathcal{E}_{\mathrm{tot}}(\hat{\omega}_{\mathcal{A}}(\beta);\hat{H}) = 0$, i.e.,

$$\left(1 - \frac{\beta}{\beta^\star}\right)\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} = 0. \tag{B10}$$

Since $\frac{\mathrm{d}\mathfrak{E}_{\mathcal{A}}}{\mathrm{d}\beta} < 0$, we arrive at the conclusion that the bound (68) is attained at a value of $\beta$ such that

$$\beta^\star(\beta) = \beta, \tag{B11}$$

which proves the thesis. ■


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