Entropy production in a photovoltaic cell

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We evaluate entropy production in a photovoltaic cell that is modeled by four electronic levels resonantly coupled to thermally populated field modes at different temperatures. We use a formalism recently proposed, the so-called multiple parallel worlds, to consistently address the nonlinearity of entropy in terms of density matrix. Our result shows that entropy production is the difference between two flows: a semiclassical flow that linearly depends on occupational probabilities, and another flow that depends nonlinearly on quantum coherence and has no semiclassical analog. We show that entropy production in the cells depends on environmentally induced decoherence time and energy detuning. We characterize regimes where reversal flow of information takes place from a cold to hot bath. Interestingly, we identify a lower bound on entropy production, which sets limitations on the statistics of dissipated heat in the cells.

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I. INTRODUCTION

In the past decade a number of physical quantities, such as charge and spin, have been accurately measured in quantum systems [1–3], and these measurements have found practical applications in superfast computation and supersecure communication [4,5]. More recently, in making use of superconducting qubits and transport by tunneling [6,7], heat dissipation had also been successfully measured in quantum devices [8–10], although yet in the absence of full quantum features [11,12]. Industrial photocell technology has reached a saturation in the efficiency of converting solar energy to electricity, and by recent quantum control of heat flow these cells achieve higher efficiencies [13].

All these indicate how important it is to understand a *consistent* theory for quantum thermodynamics. The ultimate goal of such a theory is to introduce possible correspondences between information and physical quantities. These correspondences are the textbook laws of thermodynamics in deterministic classical systems. In stochastic systems [14–18], however, they are a set of relations such as the Jarzynski inequality [19] and the Crook fluctuation theorem [20]. In quantum devices the existence of universal correspondences between information and physics are a subject of research. Here we study the correspondence for entropy as an informational measure.

Entropy is one of the central quantities, whose consistent evaluation in quantum theory is obscure due to its nonlinear dependence on the density matrix; $S = -k_B \mathrm{Tr}\hat{\rho}\ln\hat{\rho}$, with $\hat{\rho}$ being the density matrix. This quantity is one of the fundamental characteristics for quantifying many-body correlations and proved useful in critical phenomena, quantum quenches, topologically ordered states, strongly correlated systems, etc. [21]. In quantum information theory entropy helps to identify sources of fidelity loss [22]. Standard time-evolution formalisms in open quantum systems [23,24] that allow one to compute density matrices at different times are useless in evaluating entropy due to its nonlinear dependence on the density matrix [25,26]. Recently some progress has been made to consistently evaluate it in the weak-coupling regime [27] using the so-called *extended Keldysh technique on multiple parallel worlds* [28–30]. In this terminology the system of interest and whatever is coupled to it make a *world*. This evaluation beyond perturbation theory is still an open problem [31].

We previously calculated entropy production in simple examples of quantum heat engines [28–30,32]. A quantum heat engine (QHE) is a small quantum system with a number of energy levels that are coupled to several heat reservoirs. These devices are known for converting incoherent photons of thermal environments into coherent emissions [33]. Our results for simple QHEs showed that entropy flow has two parts: (1) an incoherent part, which linearly depends on the quantum system density matrix, and (2) a coherent part, which is nonlinear. Given that both parts depend on the density matrix, the reason for using this terminology, the first place being Ref. [29], has been that the nonlinear part is independent of occupation probabilities and depends only on the quantum coherence element of the density matrix as a result of the coherent drive. Interestingly, this part has no semiclassical analog. Separately, we showed in Ref. [30] that the total flow of entropy, which is the difference between these two parts, corresponds exactly to physical quantities, more precisely, to the full counting statistics of energy fluctuations [30]. This correspondence is conceptually the analog of the *second law* for a quantum theory for thermodynamics, but it is limited to the weak-coupling limits. Although the information content in the incoherent part is carried out by standard correlations, the so-called Kubo-Martin-Schwinger (KMS) correlations [34], in the coherent part it indicates a large class of correlators that exists beyond the standard ones, the so-called *extended* KMS correlations [29].

In this paper we evaluate entropy flow for a practical QHE model compared to the simple modeled we previously studied. There are a number of QHE models that resemble interesting physical phenomena, such as light-harvesting biocells [35,36], photovoltaic cells [13,37,38], and lasing heat engines [39]. Our system of interest is the QHE introduced by Scully *et al.* [13], which has four energy levels, two nearly degenerate ground states, and two excited states, and is weakly coupled to two large heat baths kept at different temperatures T_c and T_h (see Fig. 1). This QHE is externally driven by a frequency that is almost equal to the energy difference of excited states. The statistics of energy dissipations for this QHE have been

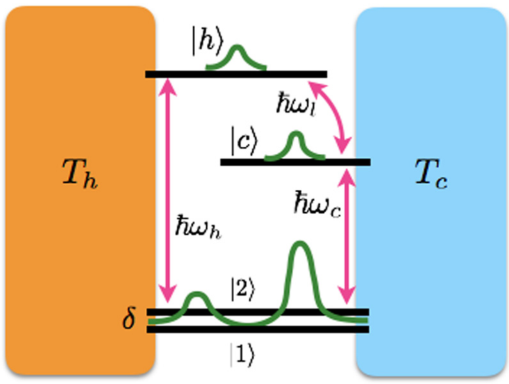

FIG. 1. A quantum heat engine with near-degenerate ground states $|1\rangle$ and $|2\rangle$, and excited states $|h\rangle$ and $|c\rangle$, that resonantly (with frequency ω_l) is coupled to two large heat baths kept at temperatures T_c and T_h. Typical occupation probabilities are represented in green.

previously studied in Ref. [40] and shown to be non-Poissonian, from which various cumulants of energy exchanges can be extracted. In this QHE several phenomena have been studied, such as lasing without inversion [41], work extraction from a single thermal reservoir [42], and elevated output powers [13]. Here, the main reason we evaluate entropy flow is to understand how to link energy fluctuations and entropy, and if the engine performs any sign of quantum thermodynamics beyond classical limits.

Our result shows interesting features in the entropy flow. We find that the presence of nonlinear flow can make entropy production in photovoltaic cells much slower or much faster than the semiclassical rate. We also study how decoherence time, which is induced by environments [43], and energy detuning, as a result of lifting degeneracy, affect the net entropy flow. By designing a QHE with lower decoherence time, we can speed up the flow of entropy between hot and cold baths. Lifting the degeneracy will result in the suppression of nonlinear flow that is the direct consequence of quantum coherence reduction. Finally, we obtain a lower bound on entropy flow as a direct result of nonlinearity in the flow.

In Sec. II we discuss the Hamiltonian and the entropy evaluation to become prepared for Sec. III, where we compute the flow in a four-level QHE. Results are briefly discussed in Sec. IV, and some details can be found in Appendixes A and B.

II. THE MODEL AND FORMALISM

In this section, after introducing the Hamiltonian model and the time evolution of the density matrix, we explain how entropy, whose evaluation requires time evolution of nonlinear operator, is consistently evaluated.

A. The Hamiltonian

Let us consider a QHE with quantum states $|x\rangle$ corresponding to energy eigenvalues E_x coupled to a number of heat baths labeled by α. The Hamiltonian of this system is $H = H_0 + H_{\rm int}$, with the noninteracting part H_0 being $H_{\rm sys} + \sum_\alpha H_\alpha$ with the following system and reservoir Hamiltonians:

$$\hat{H}_{\rm sys} = \sum_x E_x |x\rangle\langle x|,$$
$$\hat{H}_\alpha = \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q},\alpha} \hat{b}^\dagger_{\boldsymbol{q},\alpha}\hat{b}_{\boldsymbol{q},\alpha}, \tag{1}$$

and with $\hat{b}_{\boldsymbol{q},\alpha}$ ($\hat{b}^\dagger_{\boldsymbol{q},\alpha}$) being an annihilation (creation) photon operator with momentum $\boldsymbol{q}$ in the reservoir α. The interaction Hamiltonian is

$$\hat{H}_{\rm int} = \sum_\alpha \sum_{xx'} |x\rangle\langle x'|X^{(\alpha)}_{xx'}(t),$$
$$\hat{X}^{(\alpha)}_{xx'}(t) = \hbar \sum_{\boldsymbol{q}} c_{xx',\boldsymbol{q}\alpha}\hat{b}_{\boldsymbol{q}\alpha}\exp(-i\omega_{\boldsymbol{q}\alpha}t) + {\rm H.c.}, \tag{2}$$

with the $\hat{X}$ operator acting on heat baths, and the complex-valued $c_{xy,q\alpha}$ that couples the transition $x \to x'$ to a photon of certain momentum in a heat bath. The coefficient $\exp(\pm i\omega_{\boldsymbol{q}\alpha}t)$ shows the time dependence of the creation and annihilation operators. We assume adiabatic switching on interaction such that far in the past $t \to -\infty$, all couplings are absent; therefore the total density matrix is separable into subsystems. As the couplings slowly grow, the density matrix can be formally determined from [23]

$$\hat{\rho}(t) = Te^{i\int_\infty^t d\tau \hat{H}_{\rm int}(\tau)}\hat{\rho}(-\infty)\bar{T}e^{i\int_{-\infty}^t d\tau \hat{H}_{\rm int}(\tau)}, \tag{3}$$

with T ($\bar{T}$) being (anti-) time ordering operator. One can expand Eq. (3) in terms of $\hat{X}$ operators. The Keldysh formalism [24] is a general method to evaluate all energy orders [24,44], for which the Keldysh contour is considered to represent the evolution of bra and ket states at different times; i.e., the ket (bra) states evolve along (opposite to) the time flow. Details can be found in Ref. [27].

B. Entropy

As mentioned above, entropy is nonlinear in the density matrix of *world*. Let us consider that in a world with the density matrix ρ_w consisting of several systems and heat baths, the system of interest has the partial density matrix $\hat{\rho}$. The entropy of this system is $S = -{\rm Tr}\hat{\rho}\ln\hat{\rho}$ and is evaluated by tracing out all except the system of interest. Here we assume $k_B = 1$. This logarithmic dependence makes the evaluation of entropy mathematically involved.

Consider the simple example that interactions are so weak that the quantum system is perturbed only in the vicinity of its equilibrium state at ground state. In this case the density matrix can be approximated to $\rho(t) \approx p_0 + \rho^{(1)}(t)$, with $|\rho^{(1)}/p_0| \ll 1$. The entropy flow, i.e., $F = dS/dt$, becomes $-(1+\ln p_0)d\rho^{(1)}/dt - (1/2p_0)d(\rho^{(1)})^2/dt + \cdots$, which is clearly nonlinear in the density matrix. We showed in Ref. [29] that for any positive n one can show $d(\rho)^n/dt \neq n(\rho^{n-1})d\rho/dt$. In other words, one cannot simplify $-(1/2p_0)d(\rho^{(1)})^2/dt$ to $-p_0 d\rho^{(1)}/dt$. Such a simplification is only meaningful for noninteracting systems.

First one must notice that in the logarithmic expansion of entropy there are infinite terms to be computed. This is impossible and, moreover, we cannot find any clear criteria to make a meaningful truncation on the expansion. Nazarov in Ref. [27] suggested that we rewrite entropy as a limit of the Renyi entropies [45], i.e., $S = -\lim_{M\to 1} dS_M/dM$, with the Renyi entropy of positive degree M being $S_M = \mathrm{Tr}\{\rho\}^M$. Naturally computing the Renyi entropy flows is the next problem to achieve (see Appendix A). We proposed in Ref. [29] how to compute the time evolution of the operator $\{\hat{\rho}\}^M(t)$ without using the solution of $\hat{\rho}$. In order to evaluate the entropy flow in a quantum system one should evaluate the Renyi entropy flow and analytically continue it to $M \to 1$. Detailed analysis shows that the consistent entropy flow has two parts, Q_i and Q_c:

$$\frac{dS}{dt} = \frac{Q_i - Q_c}{T}$$
$$Q_i = \sum_{x'yy'} \rho_{x'y}\tilde{\chi}_{y'x',yy'}(\omega_{yy'})(\bar{n}(\omega_{yy'})+1)\omega_{yy'}$$
$$Q_c = \sum_{xx'yy'} \rho_{x'x}\rho_{y'y}\tilde{\chi}_{xx',yy'}(\omega_{yy'})\omega_{yy'}, \quad (4)$$

with Q_i being the incoherent flow of entropy and Q_c the coherent part. $\hbar\omega_{yy'} \equiv E_y - E_{y'}$ and $\tilde{\chi}_{xx',yy'}$ represent the generalized dynamical susceptibility between two transitions: $|x\rangle \to |x'\rangle$ and $|y\rangle \to |y'\rangle$. $\bar{n}$ denotes the Bose distribution.

Equation (4) has two parts: (1) the incoherent flow Q_i, which is linearly proportional to the reduced density matrix, and (2) the coherent part Q_c, which is nonlinear—in fact, quadratic, because we calculate it in the second-order perturbation theory. This entropy flow can be equivalently determined from using the corresponding physical quantities, which are the full counting statistics of energy transfers (see Appendix B).

III. FOUR-LEVEL QUANTUM HEAT ENGINES

Let us calculate entropy flow in the four-level QHE introduced by Scully *et al.* [13] and shown in Fig. 1. This QHE consists of two nearly degenerate lower levels $|1\rangle$ and $|2\rangle$ (denoted by label $i,j = 1,2$) with energy $E_1 = E_2 + \delta$ and δ being energy detuning, and two excited levels $|h\rangle$ and $|c\rangle$ with energies E_h and E_c (denoted by labels $\alpha = h,c$) (see Fig. 1). An example of such a QHE is a laser heat engine in which environmental noise helps to increase the net emitted laser. The full counting statistics of energy transfers in this QHE have been calculated in Ref. [40]. By applying the first cumulant of the energy statistics in the second law (as we will show in next section) we can immediately determine a semiclassical value for the entropy flow. However, here we calculate it using a formalism that is free of any assumption about the underlying quantum thermodynamics. Therefore we notice that our results are dramatically different from what a semiclassical approach predicts.

Here we choose the probe environment to be the hot bath with temperature T_h. The quantum system is externally driven by a single-mode cavity at the frequency $\omega_l \approx (E_h - E_c)/\hbar$. The driving Hamiltonian is $\hat{H}_{sys-dr} = \Omega(\hat{b}_l^\dagger|c\rangle\langle h| + \hat{b}_l|h\rangle\langle c|)$,$\hat{b}_l$ ($\hat{b}_l^\dagger$) being the annihilation (creation) operator for the cavity mode; $\langle\hat{b}_l^\dagger\hat{b}_l\rangle = \bar{n}_l$; $\langle\hat{b}_l\hat{b}_l^\dagger\rangle = \tilde{n}_l$ with $\bar{n}_l$ being the average number of photons in the cavity and $\tilde{n}_l \equiv \bar{n}_l + 1$ [13,41].

The stationary density matrix solution can be summarized in the vector $\boldsymbol{R} = \{\rho_{11},\rho_{22},\rho_{hh},\rho_{cc},\mathrm{Re}(\rho_{12})\}$. This vector can be evaluated using the time-evolution equation $d\boldsymbol{R}/dt = \mathscr{L}\boldsymbol{R}$ by assuming that the density matrix slowly varies (Markov approximation); thus we approximate $\rho(t-t') \approx \rho(t)$. One can determine the following $\mathscr{L}$ for the dynamics:

$$\mathscr{L} \equiv \begin{pmatrix} \chi_{11} & 0 & \tilde{\chi}_{h1}\tilde{n}_h & \tilde{\chi}_{c1}\tilde{n}_c & -2\tilde{\chi}_{12} \\ 0 & \chi_{22} & \tilde{\chi}_{h2}\tilde{n}_h & \tilde{\chi}_{c2}\tilde{n}_c & -2\tilde{\chi}_{12} \\ \tilde{\chi}_{h1}\bar{n}_h & \tilde{\chi}_{h2}\bar{n}_h & \chi_{hh} & \Omega^2 n_l & 2\tilde{\chi}_{1h,h2}\bar{n}_h \\ \tilde{\chi}_{c1}\bar{n}_c & \tilde{\chi}_{c2}\bar{n}_c & \Omega^2\tilde{n}_l & \chi_{cc} & 2\tilde{\chi}_{1c,c2}\bar{n}_c \\ -\tilde{\chi}_{12} & -\tilde{\chi}_{12} & \tilde{\chi}_{1h,h2}\tilde{n}_h & \tilde{\chi}_{1c,c2}\tilde{n}_c & \chi \end{pmatrix}, \quad (5)$$

with coupling χ_{ii} being $-\sum_\alpha \tilde{\chi}_{i\alpha,\alpha i}\bar{n}_i$; χ_{hh} being $-\sum_i \tilde{\chi}_{ih,hi}\tilde{n}_h - \tilde{n}_l\Omega^2$; χ_{cc} being $-\sum_i \tilde{\chi}_{ic,ci}\tilde{n}_c - \bar{n}_l\Omega^2$; χ being $-(1/2)\sum_{i,\alpha}\tilde{\chi}_{i\alpha,\alpha i}\bar{n}_\alpha - 1/\tau_2$; and the symmetric χ_{ij} being $(1/2)\sum_\alpha \tilde{\chi}_{i\alpha,\alpha j}\bar{n}_\alpha$ for $i \neq j$.

This evolution equation has been solved explicitly (see Eq. (S26) of the Supplemental Materials in Ref. [13]). One should notice that χ depends on decoherence time τ_2, which is induced by environment and affects all elements of the system density matrix, including an exponential decay of the imaginary part of the coherence $\mathrm{Im}\rho_{12} \approx \exp(-t/\tau_2)$.

Being equipped with the stationary solution for $\boldsymbol{R}$, we can now compute the entropy flow by substituting it in Eq. (4). The result is that the stationary flow of entropy from the probe (hot) heat bath becomes

$$\frac{dS}{dt} = \Bigg\{\gamma p_h - E_{h2}\tilde{\chi}_{h2}\bar{n}\left(\frac{E_{h2}}{T_h}\right)p_2 - E_{h1}\tilde{\chi}_{h1}\bar{n}\left(\frac{E_{h1}}{T_h}\right)p_1$$
$$- \tilde{\chi}_{1h,h2}\left[E_{h1}\bar{n}\left(\frac{E_{h1}}{T_h}\right) + E_{h2}\bar{n}\left(\frac{E_{h2}}{T_h}\right)\right]\mathrm{Re}\rho_{12}$$
$$- \frac{1}{2}\sum_{i=1,2} E_{hi}\tilde{\chi}_{1h,h2}|\rho_{12}|^2\Bigg\}/T_h, \quad (6)$$

with $p_x \equiv \rho_{xx}$ for x being 1,2,H.c., $\tilde{\chi}_{\alpha i} \equiv \tilde{\chi}_{i\alpha,\alpha i}(\omega_{i\alpha})$ being the dynamical response function, and $\tilde{\chi}_{1\alpha,\alpha 2} = \sqrt{\tilde{\chi}_{\alpha 1}\tilde{\chi}_{\alpha 2}}$. Moreover, $\gamma \equiv \sum_{i=1,2}[\bar{n}(E_{hi}/T_h)+1]E_{hi}\tilde{\chi}_{hi}$. Equivalently, one can compute the flow of entropy by using its corresponding full counting statistics of energy transfers in Eq. (B1).

In Eq. (6) the linear terms determine incoherent flow, where the first term is the entropy gain by photon absorption and the next three terms are entropy loss in photon decays. The quadratic term is the coherent flow that is the entropy loss due to extended KMS correlators.

Before discussing results, let us briefly show how one can derive the incoherent part independently using the combination of textbook second law and the statistics of energy transfers worked out in Ref. [40]. The full counting statistics generating function of energy E_{tr} being exchanged during time interval $\mathcal{T}$ is $G(\xi,t) = \mathrm{Tr}\rho(\xi,t)$, with $\rho(\xi,t)$ being the stationary solution of $d\rho(\xi,t)/dt = \mathscr{L}(\xi)\rho(\xi,t)$, with ξ being the characteristic parameter. The explicit form of $\mathscr{L}(\xi)$ is given by Eq. (14) of Ref. [40]. This generating function determines the first cumulant $d\langle E\rangle/dt$. By substituting it in the relation between entropy and energy flows $dS/dt = (1/T)dE/dt$, one can exactly obtain the first two lines of Eq. (6). However, it

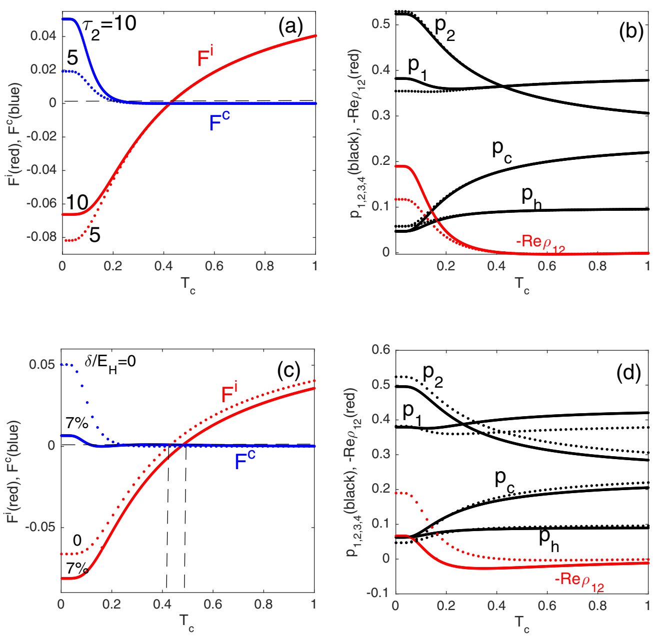

FIG. 2. Incoherent (red) and coherent (blue) entropy flows in a hot (probe) environment versus cold-bath temperature T_c for (a) two different values of decoherence time $\tau_2 = 5$ (dotted) and 10 (solid) and the absence of detuning energy. (c) Two different values of detuning $\delta/E_{h1} = 0$ (dotted) and 7% (solid) both for the case of longer detuning time $\tau_2 = 10$. (b,d) The corresponding p_1, p_2, p_c, p_h (black) and $-\mathrm{Re}\rho_{12}$ (red) with the same order for dotted and solid lines. Other parameters are $E_h = 1.5, E_c = 0.4, E_1 = E_2 = 0.1, T_h = \Omega/2 = n_l = \tilde{\chi}_{h1} = \tilde{\chi}_{h2} = \tilde{\chi}_{c2} = 10\tilde{\chi}_{c1} = 1$.

is important to notice that the second law is unable to provide the complete flow of entropy with coherent flow included.

Let us consider two QHEs with no energy detuning, i.e., $\delta = 0$, and for two different values of decoherence time, i.e., $\tau_2 = 5$ (dotted) and 10 (solid). The incoherent (coherent) entropy flows F^i (F^c) in the probe environment depend on the temperature of the cold environment T_c. This dependence is plotted in Figs. 2(a)–2(d) for the couplings specified in the caption. The net entropy is $F = F^i - F^c$, as shown in Eq. (4).

At low $T_c \ll T_h$, Fig. 2(a) indicates that entropy flows out of the hot bath. By warming up the cold bath above the *onset* temperature $T_o > 0.42$ the overall ground-state populations, as shown in panel (b), are suppressed and the excited states become more populated. This causes the *reversal* flow of entropy from the cold to the hot bath. At the onset temperature there is no flow of entropy expected. As shown, the onset temperature does not depend on decoherence time. Let us now compare the net entropy flow $F = F^i - F^c$ determined from the consistent formalism and the semiclassical flow predicted by the second law, which is equivalent to the incoherent part F^i. One can see in Fig. 2(a) that the net flow is heavily suppressed. This suppression takes place due to the contribution of the nonlinear (coherent) part of the flow that is quadratic in ρ_{12} and is as important as the semiclassical part where ρ_{12} is not negligible. Moreover, at the low T_c limit, the smaller the decoherence time τ_2, the faster entropy flows out of the probe environment.

Now let us study the effect of energy detuning on entropy flow. Figure 2(c) shows incoherent (coherent) entropy flow F^i (F^c) for two QHEs with detuning ratio $\delta/E_{h2} = 0$ (dotted) and 7% (solid). Panel (d) shows the corresponding stationary populations and coherence. By increasing the energy detuning the onset temperature becomes larger. This is mostly because of a sign change in $\mathrm{Re}\rho_{12}$ in the presence of detuning, which in Eq. (6) makes the linear term on $\mathrm{Re}\rho_{12}$ turn from positive at low T_c to negative at higher T_c, and this reduces the total entropy flow and causes a shift of the onset temperature forward.

Now let us simplify the entropy flow for the cold bath being at zero temperature limit. One can see in Fig. 2 that at zero T_c both parts of entropy flow are at their extrema and with opposite signs. We use Eq. (6) and analytically compute the flow for an engine with zero detuning. One can simplify the time evolution of p_1 and p_2 in the limit of $T_c \approx 0$ using Eq. (5). Some lines of algebraic calculations show that the stationary value of the ground-state occupation probabilities under such conditions is $p_i = p_h \exp(E_H/k_B T_h) + [\eta_i/\bar{n}(E_H/T_h)]p_c - \lambda_i \mathrm{Re}\rho_{12}$, with η_i being $\tilde{\chi}_{ci}/\tilde{\chi}_{hi}$, $\lambda_1 = \sqrt{r_h}$, $\lambda_2 = 1/\lambda_1$, $E_H \equiv E_{hi}$, and $r_h \equiv \tilde{\chi}_{h2}/\tilde{\chi}_{h1}$. Substituting them all in the entropy flow of Eq. (6) will determine the entropy flow for the QHE:

$$\left.\frac{dS}{dt}\right|_{T_c \approx 0} = -\frac{E_H}{k_B T_h}[p_c(\tilde{\chi}_{c1} + \tilde{\chi}_{c2}) + \tilde{\chi}_{1h,h2}|\rho_{12}|^2]. \tag{7}$$

Equation (7) clearly states that the engine at zero cold-bath temperature exhibits a persistent negative flow of entropy from hot to cold bath, no matter what the other parameters are. This, at least in the weak-coupling limit, indicates no violation takes place against the third law in this engine.

Given that the entropy flow changes sign at the onset temperature, one can simplify Eq. (6) to find out the condition where reversal flow occurs, which is,

$$\begin{aligned}[]&[\bar{n}(E_H/T_h) + 1](1 + r_h)p_h - \bar{n}(E_H/T_h)(p_1 + r_h p_2 \\ &+ 2\sqrt{r_h}\,\mathrm{Re}\,\rho_{12}) - \sqrt{r_h}|\rho_{12}|^2 \geqslant 0,\end{aligned} \tag{8}$$

with zero flow at the onset temperature.

Before concluding, let us make some important remarks about the net entropy flow in these quantum photovoltaic cells. For devices with $r_h = 1$, by dividing both sides of Eq. (6) by $\tilde{\chi}_{h1}E_H$ and denoting the left side $f = (dS/dt)/\tilde{\chi}_{h1}E_H$, a few lines of algebra simplify the result into a quadratic equation for quantum coherence: $|\mathrm{Re}\rho_{12}|^2 + 2\bar{n}\mathrm{Re}\rho_{12} + \bar{n}(1 - p_c) - (3\bar{n} + 2)p_h + f = 0$. Solving this equation for $\mathrm{Re}\rho_{12}$ will determine the condition for it to be real-valued. One can find the forbidden zone is where $p_c + (3\bar{n} + 2)/\bar{n}\, p_h < f - \bar{n} + 1$. Given that the left side of this inequality is positive-valued, the left side cannot be negative and therefore the following lower bound on net entropy flow holds: $dS/dt \geqslant [\bar{n}(E_H/T_h) - 1]E_H\tilde{\chi}_{h1}$.

The entropy flow we obtained here for this QHE can be measured experimentally using its exact corresponding partners in physical quantities. These physical quantities are the full counting statistics of energy transfers. This interestingly indicates that the entropy lower bound reveals the existence of a corresponding constraint on energy fluctuations in the system. This can be further developed and experimentally tested.

IV. SUMMARY

We calculated the entropy flow of a four-level quantum heat engine within a weak interaction limit. The results, obtained from the full quantum formalism of multiple parallel worlds, show that in addition to semiclassical results, entropy flow has a nonlinear contribution of quantum coherence as the result of coherent drive. The presence of this nonlinear term significantly suppresses the semiclassical value for entropy; however, this heavy suppression does not allow for entropy to flow out of a cold bath at zero temperature. Thus the third law is not violated in the weak-coupling regime. We also explicitly determined that by reducing the environmentally induced decoherence time the onset temperature does not change but the flow can take place much faster. Lifting the degeneracy will result in the suppression of quantum coherence, which directly reduces the nonlinear term of entropy. Finally, we argued that the quadratic dependence of entropy flow on quantum decoherence, which is absent in semiclassical analysis, determines a lower bound on entropy flow. Given that there is an exact correspondence between entropy flow and energy fluctuations, one can expect that the lower bound on entropy flow can correspond to a constraint on energy fluctuations, which can be the subject of future research.

Let us now discuss how to measure the entropy. The entropy flow is not accessible in direct measurements as they are nonlinear functions of the density matrix. Direct measurements of the density matrix for a probe environment requires characterization of a reduced density matrix of an infinite system, which is a rather nontrivial procedure and needs the complete and precise reinitialization of the initial density matrix. Measuring entropy flow from their physical correspondence requires that some generating functions be extracted from determining statistical cumulants of transferred energy in the experimental data. The measurement procedures may be complex, yet they are doable and physical.

Our derivation was restricted to the second-order perturbative dynamics. Let us briefly explain how this physics can be extended to strong-coupling regimes. Here I describe two approaches for the development: One can use the polaron transformation [46] to incorporate the high-order system-bath interaction into the system dynamics. This transformation will change the generalized correlators of heat baths as well as the Renyi entropies. Alternatively, one can define the generalize density matrix $\mathcal{R}$ to include the density matrix of M worlds and extend the dynamical equation for $\mathcal{R}(t)$. The solution is a set of eigensolutions proportional to $\mathcal{R}(t) \approx \exp(-\Gamma t)$. In the strong-coupling limit there is no stationary solution with zero Γ; instead, the flow of Renyi entropy is $\mathscr{F}_M = \Gamma_0$, with Γ_0 being the closest eigenvalue to zero. This will help to identify the entropy flow in the limit of $M \to 1$ and is the subject of ongoing research.

APPENDIX A: RENYI ENTROPY FLOW

Evaluating Renyi entropies requires the time evolution of integer powers of the density matrix. Consider a closed system with total density matrix ρ made of two interacting systems A and B. The reduced density matrix for system A is $\rho_A = \mathrm{Tr}_B \rho$. The Renyi entropy of degree M in the system A is $\ln S_M^A = \ln \mathrm{Tr}_A\{(\rho_A)^M\}$. If the two systems do not interact, the entropies are conserved, $d \ln S_M^{A,B}/dt = 0$; however, for interacting heat baths in thermal equilibria, a steady flow of entropy is expected from one heat bath to another one. This is similar to the steady flow of charge in an electronic junction that connects two leads kept at different chemical potentials [43]. Defining the Renyi entropy flow of degree M in system A as $\mathscr{F}_M^A = d \ln S_M^A/dt$, there is a conservation law for $\mathscr{F}_M^{A+B}$; however, due to the inherent nonlinearity, $\mathscr{F}_M^A + \mathscr{F}_M^B \neq 0$, and the equality holds only approximately, subject to volume-dependent terms [27].

For the evaluation of Renyi entropy flow of degree M in the system A, i.e., $d \ln S_M^A/dt$, in the second-order perturbation we need to compute $d(\rho_A)^M/dt$. Let us drop the index A from the equation for now. Considering the initial density matrix is ρ_0, it can be found later to take the following value, $\rho(t) = \rho_0 + \rho^{(1)}(t) + O(2)$, with $\rho^{(1)} = \rho_I^{(1)} + \rho_{II}^{(1)}$ and $\rho_I^{(1)}(t) = -i \int_0^t dt' \hat{H}(t')\hat{\rho}(t)$ and $\rho_{II}^{(2)}(t) = i \int_0^t dt' \hat{\rho}(t)\hat{H}(t')$. The superscripts of the parentheses indicate perturbation order. Similarly, $d\rho/dt = \dot{\rho}^{(1)} + \dot{\rho}^{(2)} + O(3)$, with $\dot{\rho}^{(1)} = \dot{\rho}_1^{(1)} + \dot{\rho}_2^{(1)}$ and $\dot{\rho}_1^{(1)}(t) = -i \hat{H}(t)\hat{\rho}$ and $\dot{\rho}_2^{(1)}(t) = i \hat{\rho}\hat{H}(t)$ and $\dot{\rho}^{(2)} = i[\dot{\rho}^{(1)}, H]$. The flow of nonlinear measure can be expanded as follows: $d(\rho)^M/dt = (d\rho/dt)(\rho)^{M-1} + \rho(d\rho/dt)(\rho)^{M-2} + \cdots + (\rho)^{M-1}(d\rho/dt)$. Using these definitions we can evaluate $d\rho^M/dt$ in the second order as follows:

$$
\begin{aligned}
\frac{d\rho^M}{dt} &= \{\dot{\rho}^{(2)}\rho_0^{M-1} + \rho_0\dot{\rho}^{(2)}\rho_0^{M-2} + \cdots + \rho_0^{M-1}\dot{\rho}^{(2)}\} \\
&\quad + \{\dot{\rho}^{(1)}[\rho^{(1)}\rho_0^{M-2} + \rho_0\rho^{(1)}\rho_0^{M-3} + \cdots] \\
&\quad + \rho_0\dot{\rho}^{(1)}[\rho^{(1)}\rho_0^{M-3}\rho_0\rho^{(1)}\rho_0^{M-4} + \cdots] \\
&\quad + \cdots + \rho_0^{M-2}\dot{\rho}^{(1)}\rho^{(1)}\},
\end{aligned} \tag{A1}
$$

where the first line of Eq. (A1) represents photon exchanges taking place only within one world, and the remaining terms represent the exchange of photons between different copies of world density matrices.

We implement the extended Keldysh formalism for the analysis of Renyi entropy flow. Detailed analysis with all diagrams can be seen in Appendix B of [29]. Rigorous analysis shows that the Renyi entropy flow is

$$
\begin{aligned}
\mathscr{F}_M &= \sum_{yy'} \frac{M\bar{n}(M\omega_{yy'})}{\bar{n}((M-1)\omega_{yy'})\bar{n}(\omega_{yy'})\omega_{yy'}}\{Q_{yy'}^i - Q_{yy'}^c\} \\
Q_{yy'}^i &= \sum_{x'} \rho_{x'y}\tilde{\chi}_{y'x',yy'}(\omega_{yy'})(\bar{n}(\omega_{yy'}) + 1)\omega_{yy'} \\
Q_{yy'}^c &= \sum_{xx'} \rho_{x'x}\rho_{y'y}\tilde{\chi}_{xx',yy'}(\omega_{yy'})\omega_{yy'},
\end{aligned} \tag{A2}
$$

with $\hbar\omega_{yy'} \equiv E_y - E_{y'}$.

In Eq. (A2) there are two types of flows contributing: (i) the incoherent flow Q^i for quantum leaps on energy levels, and (ii) the coherent flow Q^c for the exchange of energy through the quantum coherence. Q^i does, in fact, represent the first line of Eq. (A1) and Q^c corresponds to the rest of them.

APPENDIX B: FULL COUNTING STATISTICS OF ENERGY DISSIPATIONS

This correspondence makes evaluation of the Renyi entropy flows possible using full counting statistics of energy exchanges [28]. Previously, similar correspondence was found in charge transport in Refs. [47] and [48].

Let us briefly recall what is the full counting statistics (FCS) of energy transfers between a small quantum system weakly coupled to a classical environment kept at temperature T [49]. It concentrates on the probability $\mathscr{P}^{(T)}(E_{tr},\mathcal{T})$ to have energy E_{tr} transferred between two systems during time interval $\mathcal{T}$ [49]. The superscript (T) refers to the temperature of environment. In the long $\mathcal{T}$ limit all statistical cumulants of the energy transfers can be determined from the generating function $G^{(T)}(\xi) = \int_0^T dE_{tr}\mathscr{P}^{(T)}(E_{tr},\mathcal{T})\exp(i\xi E_{tr}) \approx \exp[-\mathcal{T} f^{(T)}(\xi)]$. The parameter ξ is a characteristic parameter, and cumulants are given by expansion of $f(\xi)$ in ξ at $\xi = 0$.

The correspondence between Renyi entropy and FCS of energy transfers can be further simplified to evaluate directly the flow of von Neumann entropy between a small quantum system weakly coupled to a classical environment kept at temperature T using the following formula:

$$\frac{dS}{dt} = \lim_{M\to 1} M\left\{ f^{\left(\frac{T}{M}\right)}\left(\frac{1-M}{iT}\right) - \bar{f}^{\left(\frac{T}{M}\right)}\left(\frac{1-M}{iT}\right)\right\}. \tag{B1}$$

In the right side of Eq. (B1) there are two generating functions that should be evaluated at rescaled temperature T/M and the nonzero parameter $\xi = (1-M)/iT$; f is the generating function by means of interaction between the quantum system and the environment, where $\bar{f}$ is an auxiliary generating function statistics that carries only the coherent exchange of energy between the environment and the quantum system. To understand $\bar{f}$ let us consider that the interaction Hamiltonian is $\hat{H} = \hat{X}\hat{Y}$, with $\hat{X}$ acting on the classical environment and $\hat{Y}$ on the quantum system. This FCS generating function is associated to a Hamiltonian in which averaging takes place over the system part, i.e., $\hat{Y} \to \langle\hat{Y}\rangle$. This will be the Hamiltonian of the equilibrium system subject to time-dependent external forces. In Ref. [30] we discussed the physical realization of the scheme. We showed that Eq. (B1) can provides the textbook second law of thermodynamics in the absence of quantum coherence.

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