



Thermodynamic bounds on work extraction from photocells and photosynthesis

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Abstract We put forward a unified thermodynamic analysis of generic minimal models of solar-powered cyclic processes that can be viewed as quantum heat engines. The resulting general efficiency bound for work production is consistent with the second law of thermodynamics if it allows for heat and entropy generation. This bound is shown to interpolate between the Carnot and the Shockley–Queisser bounds. Power boost induced by coherence or multiexciton generation does not affect the efficiency. These features may allow us to design solar-pumped schemes that are optimal, both energetically and operationally.

1 Introduction

The twenty-first century still predominantly relies on nineteenth century thermodynamic cycles to generate power: internal combustion engines, nuclear or fossil-fuel power plants as well as solar cells or thermoelectric devices constitute diverse forms of cyclic heat machines. Because of the prominence of solar energy, it is important to evaluate the performance bounds of solar-powered devices according to the principles of heat machines, particularly since Scully et al. have proposed that solar-generated power may be boosted by quantum coherence [1–3]. We here present a unified treatment of solar devices that derives and clarifies their *universal efficiency and power bounds*, identifies their *minimal required ingredients* and elucidates the effect of optional (additional) ingredients. We thereby aim at dispelling the existing ambiguity on key issues related to this subject [4–15].

Part of the existing ambiguity is reflected by the solar-cell efficiency, which has been the subject of alternative definitions: (a) one is the *fraction of solar photons that may be converted into photoelectrons*, which is limited in p–n junctions by the Shockley–Queisser (SQ) bound [4]. The underlying assumption is that the efficiency for conversion of photons into excitons is zero for photon energies below the energy gap and 100% above it. This assumption and the tendency of photon energy in excess of the energy gap to be dissipated as heat (by exciting phonons) sets the SQ bound on the conversion efficiency of a single-junction solar cell [4]. (b)

An alternative [16] that may allow us to surpass this SQ bound [4, 16] is based on carrier multiplication, in which the absorption of a single photon produces multiple excitons and hence the *quantum efficiency* (QE) becomes *greater than 100%*. (c) Another definition is the *thermodynamic efficiency* of the solar-cell, which is *viewed as a heat engine* that generates electric work when the photoelectrons are subject to bias voltage across the p–n junction and to phonon-induced resistivity across the contacts. The standard Carnot bound of this efficiency is determined by the temperatures of the hot solar-radiation and the cold (ambient) phonon bath [1, 5]. Another issue is how to account for quantum coherence among the levels of charge-donor quantum dots that has been proposed by Scully et al. [1] as a way of enhancing the power output of solar devices, or their photosynthesis yield [13]?

The ambiguity concerning the rapport between solar-cell performance and that of heat engines can only be fully dispelled upon answering the question: how are the solar-cell QE or the SQ bound related to the *work efficiency* of a heat engine? This question is all the more crucial for heat engines that may benefit from quantum features such as coherence and entanglement [1], which call for an elucidation of the *division of the absorbed photon energy into heat and work* [17–22]. Unless these issues are resolved, we cannot optimize solar-pumped nanodevices or attain in-depth understanding of photosynthesis as a thermodynamic cycle which has been extensively debated [1, 2, 5–12].

To this end, we shall use the concept of *non-passivity* [17–19] to decompose the energy of a non-passive state

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into ergotropy and passive energy. Ergotropy is the maximum amount of work that can be extracted from a non-passive state by means of unitary transformations, while passive energy cannot be extracted in the form of useful work [23]. These concepts help us to evaluate the fraction of solar-energy input that is transformed into *proper work* upon subtracting the heat and entropy production in the process, due to its *effective resistance*. We shall thereby account for the *nonequilibrium quantum aspects* of the thermodynamic processes which are largely uncharted territory in the context of solar-powered devices.

2 Donor–acceptor quantum heat engine (QHE)

Various models have been proposed to analyse the charge separation and energy transfer in photosynthetic antennae and reaction centers. As a minimal model of a solar-powered heat engine, we consider the photoinduced charge separation between the donor (D) and the acceptor (A) molecules or quantum dots interacting with thermal radiation (Fig. 1a). Here we consider that both the donor and acceptor molecules are modelled by two level systems; $g_D(g_A)$ and $e_D(e_A)$ are the ground and excited states of the donor and acceptor molecules. Therefore the model conforms to (Fig. 1b) the generic four-level QHE scheme [2]. State b (“bottom”) corresponds to the lowest energy configuration where both molecules are in the ground states. State d describes the configuration where donor D is excited (both the excited electron and the hole are in donor D); c is a charge-separated state with the electron in acceptor A and the hole in donor D, or a conduction level in the PV case. Finally, v is the ionized state wherein the electron is transferred to a “sink” and the system is positively charged, followed by recombination $v \rightarrow b$ that closes the cycle. For further details about the donor–acceptor QHE model we refer to Ref. [2].

The considered cycle consists of 4 steps or stages: (1) following the absorption of a solar photon, the excited electron is promoted from b to d . This step is characterized by the average occupation number of solar photons at energy $E_{db} = E_d - E_b$, $\bar{n}_h = \frac{1}{\exp(\frac{E_{db}}{k_B T_h}) - 1}$. (2) In the second step, the excited electron is transferred to c with the excess energy radiated as a phonon into a bath whose average occupation phonon number at energy $E_{dc} = E_d - E_c$ is $\bar{n}_p = \frac{1}{\exp(\frac{E_{dc}}{k_B T_p}) - 1}$. (3) In the third step, the electron released from state c contributes to a charge flow (current) from c to v , following its relaxation at a rate Γ , so that the current

$$j_{cv} = e\Gamma[(\bar{n}_a + 1)\rho_{cc} - \bar{n}_a\rho_{vv}], \quad (1)$$

is governed by the populations of c and v , and the average occupation number of the bath at the ambient temperature T_a , $\bar{n}_a = \frac{1}{\exp(\frac{E_{cv}}{k_B T_a}) - 1}$. (4) To complete the

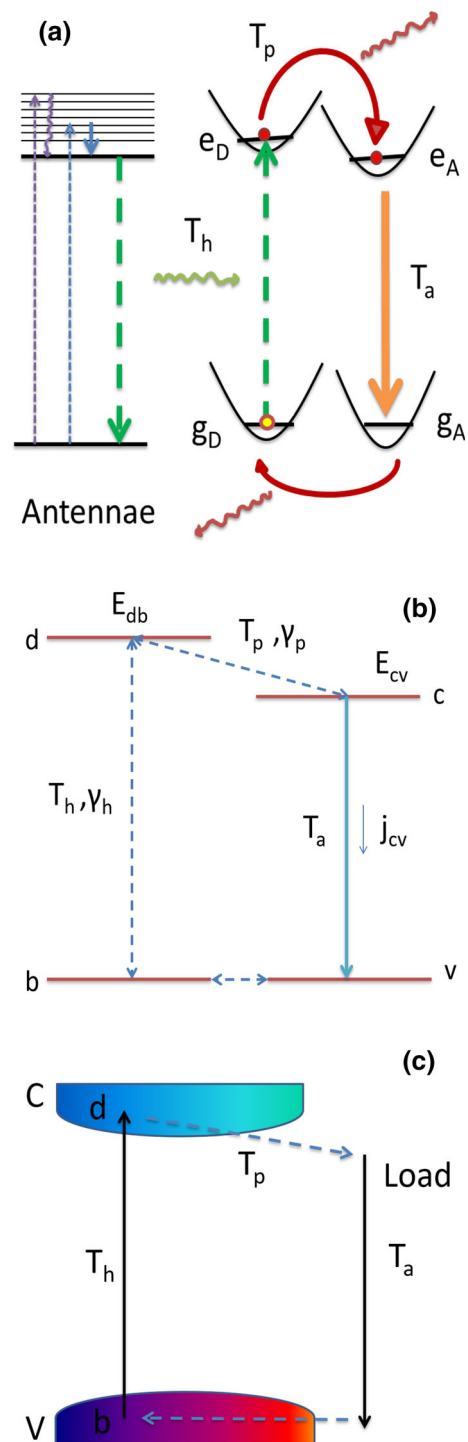


Fig. 1 **a** Scheme of charge separation between donor (D) and acceptor (A) molecules. The broad solar spectrum is absorbed by the antennae complex which undergoes rapid thermalization due to phonon scattering and reaches the bottom of the electronic band. The excitation is transferred to the reaction center represented by donor and acceptor molecules, resulting in charge separation followed by thermal relaxation that closes the cycle [2]. **b** Generic four-level quantum heat engine (QHE). **c** Analogous process in a photovoltaic solar cell combined with a p–n junction

cycle, we assume that the fourth step brings the electron back to the ground state b of donor D (reversibly or irreversibly—Appendix).

Charge separation in a reaction center can be viewed as (chemical) work done by the system, analogous to the production of electric work in a photovoltaic cell, or more generally, any kind of work in a QHE. Assuming that c and v are connected to a “load”, we introduce the drop of the electrostatic potential V as the difference between μ_c and μ_v , the chemical potentials of the levels c and v .

The steady-state populations ρ_{cc}^s and ρ_{vv}^s calculated from the master (rate) equations in the Appendix yield the power delivered to the load as $P = j_{cv}V$ upon using Eq. (1). By increasing Γ one can change the operation from the open-circuit ($\Gamma = 0, V = V_{OC}, j_{cv} = 0$) to the short-circuit regime.

Even if the $c \rightarrow v$ transition is viewed as a coherent or non-dissipative process, under the action of some bias potential V_{bias} , its coherence must be eventually destroyed by the load according to Kirchoff’s law. Hence, in a cyclic heat engine, Eq. (1) with $\Gamma \neq 0$ is appropriate.

3 Work production

The maximum useful work W that can be done by the system when the electron undergoes the transition from c to v is equal to the change in the total energy from which the change in *passive energy* (heat) must be deducted? [17–22]

$$W = \underbrace{eV}_{\text{Work(non-passivity)}} = \underbrace{E_{cv}}_{\text{energy}} - \underbrace{T_a \Delta S_{c \rightarrow v}}_{\text{heat(passivity)}}, \quad (2a)$$

where

$$\Delta S_{c \rightarrow v} = k_B \ln \left(\frac{\rho_{vv}}{\rho_{cc}} \right), \quad (2b)$$

is the change in the entropy of the system when the electron undergoes the $c \rightarrow v$ transition. Only if $|c\rangle$ and $|v\rangle$ correspond to equilibrium states, W in (2a) can be identified with the change in the Helmholtz free energy [24]. Note that $\Delta S_{c \rightarrow v}$ can only be negative if there is *population inversion* between levels c and v , in which case non-passivity *increases* as a result of the transition.

On the other hand, the total entropy change ΔS_{tot} in the cycle must be positive-definite according to Spohn’s rendition of the second (Clausius) law of thermodynamics [25], which requires (assuming $v \rightarrow b$ recombination to be reversible)

$$\Delta S_{tot} = \Delta S_{b \rightarrow d} + \Delta S_{d \rightarrow c} + \Delta S_{c \rightarrow v} \geq 0. \quad (3)$$

In analysing the inequality (3), we may allow for phonon temperature T_p (inside the junction) that differs from the ambient temperature T_a at the load (out-

side the junction) (Fig. 1c). Then $\Delta S_{b \rightarrow d} = E_{bd}/T_h$ and $\Delta S_{d \rightarrow c} = E_{dc}/T_p$ respectively. The total change in the system’s entropy is (partially) compensated by $\Delta S_{c \rightarrow v}$. Full compensation of the entropy change in a cycle occurs in the open-circuit limit $j_{cv} \rightarrow 0, \Gamma \rightarrow 0$ which corresponds to

$$\begin{aligned} \Delta S_{c \rightarrow v} &= -[\Delta S_{b \rightarrow d} + \Delta S_{d \rightarrow c}] \\ &= \left[\frac{E_{db}}{T_h} - \frac{E_{dc}}{T_p} \right]. \end{aligned} \quad (4)$$

In what follows we analyse the rate of passivity increase according to Eq. (2a), so as to estimate the maximum amount of work extracted from an engine upon accounting for the heat and entropy flux.

4 Heat and entropy production

The steady-state energy flow through the system

$$\dot{E}_{t=\infty} = Tr \left[\frac{d\rho_S}{dt} H_S \right], \quad (5)$$

is obtained from the master equation associated with the action of the hot-bath (h), phonon-bath (p) and ambient-bath (a) Liouville Lindblad operators \mathcal{L} :

$$\frac{d\rho_S}{dt} = (\mathcal{L}_h + \mathcal{L}_p + \mathcal{L}_a)\rho_S(t). \quad (6)$$

The heat flux from the respective bath to the system is [21, 22]

$$\begin{aligned} J_{h \rightarrow S} &= Tr [\mathcal{L}_h[\rho_S] H_S]_{t=\infty}, \\ J_{p \rightarrow S} &= Tr [\mathcal{L}_p[\rho_S] H_S]_{t=\infty}, \\ J_{a \rightarrow S} &= Tr [\mathcal{L}_a[\rho_S] H_S]_{t=\infty}, \end{aligned} \quad (7)$$

whose explicit form is given by Eq. (A12). The von-Neumann entropy increase $\dot{S} = -k_B Tr[\dot{\rho}_S \ln \rho_S]$ is related to the heat flux. Using Eq. (6) we obtain the entropy fluxes from the respective baths (h, p and a) as

$$\begin{aligned} \dot{S}_{h \rightarrow S} &= -k_B Tr [\mathcal{L}_h[\rho_S] \ln \rho_S], \\ \dot{S}_{p \rightarrow S} &= -k_B Tr [\mathcal{L}_p[\rho_S] \ln \rho_S], \\ \dot{S}_{a \rightarrow S} &= -k_B Tr [\mathcal{L}_a[\rho_S] \ln \rho_S]. \end{aligned} \quad (8)$$

We present here only the explicit form of $\dot{S}_{a \rightarrow S}$ which is important for our present purpose:

$$\dot{S}_{a \rightarrow S} = -k_B \Gamma [\bar{n}_a \rho_{vv} - (\bar{n}_a + 1) \rho_{cc}] \ln \left(\frac{\rho_{cc}}{\rho_{vv}} \right), \quad (9)$$

A particular definition of the entropy production rate was given in Ref. [12] as

$$\sigma = \dot{S} - \frac{J_{h \rightarrow S}}{T_h} - \frac{J_{p \rightarrow S}}{T_p} \geq 0, \quad (10)$$

where the entire entropy change rate of the system is $\dot{S} = \dot{S}_{h \rightarrow S} + \dot{S}_{p \rightarrow S} + \dot{S}_{a \rightarrow S}$. At steady state, this entropy production rate (blue solid line in Fig. 2a), becomes *negative* for $E_{cv} \rightarrow E_{db}$. This however contradicts the Second Law.

The problem with the definition in Eq. (10) is that it ignores the heat flux from heat engine to the outside agent at the ambient temperature, $-\frac{J_{a \rightarrow S}}{T_a}$. Instead, we redefine the minimum entropy production rate as

$$\sigma' = \dot{S} - \frac{J_{h \rightarrow S}}{T_h} - \frac{J_{p \rightarrow S}}{T_p} - \frac{J_{a \rightarrow S}}{T_a} \geq 0, \quad (11)$$

The entropy production rate σ' in the steady state (Fig. 2b—red solid line), *is always positive*. The positivity of the entropy production rate can be generally proven for Markovian processes using Spohn's analysis [25].

5 Maximum output work and power

It is *commonly assumed* [5] that the power and the efficiency can be defined as

$$\begin{aligned} P &= -[J_{h \rightarrow S} + J_{p \rightarrow S}] \Rightarrow P = -J_{a \rightarrow S} \\ \eta &= \frac{-[J_{h \rightarrow S} + J_{p \rightarrow S}]}{J_{h \rightarrow S}} \Rightarrow \eta = \frac{-J_{a \rightarrow S}}{J_{h \rightarrow S}} \end{aligned} \quad (12)$$

However, these *conventional definitions* of power and efficiency *only hold* for $T_a = 0$, whereas for finite T_a , such definitions may overestimate power and efficiency, since they do not take into account the entropy flux out of the system (Cf. Eq. (10)) that contributes to its *passivity increase*. In the following we obtain the *actual work* done by the heat engine upon allowing for the rate of entropy production as per Eq. (11).

Using Eq. (8), the output power can be obtained by the relation

$$P = -[J_{a \rightarrow S} - T_a \dot{S}_{a \rightarrow S}], \quad (13)$$

where $T_a \dot{S}_{a \rightarrow S}$ is the passivity-change contribution. This power in turn corresponds to the efficiency

$$\eta = \frac{P}{J_{h \rightarrow S}} = \frac{-[J_{a \rightarrow S} - T_a \dot{S}_{a \rightarrow S}]}{J_{h \rightarrow S}}. \quad (14)$$

6 Efficiency bound

An alternative definition for the efficiency is the ratio of the power acquired from the sun, $P_s = \frac{j_s}{e} E_{db}$, where j_s/e is the rate of generated photo-electrons, to the power extracted from the reaction center, $P = j_{cv} \cdot V$. The highest (Carnot) efficiency of a heat engine is obtained at its reversibility point, which for a dissipative $c \rightarrow v$ transition corresponds to the *zero-current limit* of Eq. (1), i.e., at the open-circuit value V_{OC} (Eq. A7): given that near the reversibility point $P = j_{cv} \cdot V_{OC}$, we have

$$\begin{aligned} \eta_{Max} &= \frac{e V_{OC}}{E_{db}} \left(\frac{j_{cv}}{j_s} \right) \\ &= \frac{E_{cv} + k_B T_a \left(\frac{E_{dc}}{k_B T_p} - \frac{E_{db}}{k_B T_h} \right)}{E_{db}} \cdot \left(\frac{j_{cv}}{j_s} \right). \end{aligned} \quad (15)$$

Under the assumption $j_s = j_{cv}$, and upon using the identity $E_{cv} = E_{db} - E_{dc}$, where each term expresses the corresponding energy difference, the maximum efficiency can be evaluated to have the general form

$$\eta_{Max} = 1 - \frac{T_a}{T_h} + \frac{E_{dc}}{E_{db}} \left(\frac{T_a}{T_p} - 1 \right). \quad (16)$$

This equation is our central result. In order to be consistent with the second law, we choose T_a to be the lowest of all bath temperatures, i.e., $T_a \leq T_p < T_h$. The above efficiency is then invariably bounded by its Carnot bound

$$\eta_{Max} \leq 1 - \frac{T_a}{T_h} := \eta_{Carnot} \quad (17)$$

We can now compare the Carnot bound η_{Carnot} , the Schockley–Queisser (SQ) bound η_{SQ} evaluated for $T_a \rightarrow 0$, and η_{Max} . The highest efficiency bound is attained as $T_a \rightarrow 0$, where η_{Max} is bounded by

$$\eta_{Max} \xrightarrow{T_a \rightarrow 0} \eta_{SQ} = \frac{E_{cv}}{E_{db}} \leq \eta_{Carnot}(T_a = 0) = 1. \quad (18)$$

When $E_{cv} \rightarrow E_{db}$, we have $\eta_{SQ} \rightarrow 1$. On the contrary, the lowest efficiency bound is

$$\eta_{Max} = 1 - \frac{T_p}{T_h}; \Leftrightarrow T_a = T_p; \quad (19)$$

whereas $\eta_{SQ} = 0$ when $E_{cv} = 0$. Hence, we conclude that at $T_a = 0$, SQ is the relevant efficiency bound while at a higher temperature, $T_a = T_p$, Carnot serves as a tighter bound for the machine performance. In general, one should interpolate between these bounds according to Eq. (16) in order to find η_{Max} (Fig. 2b).

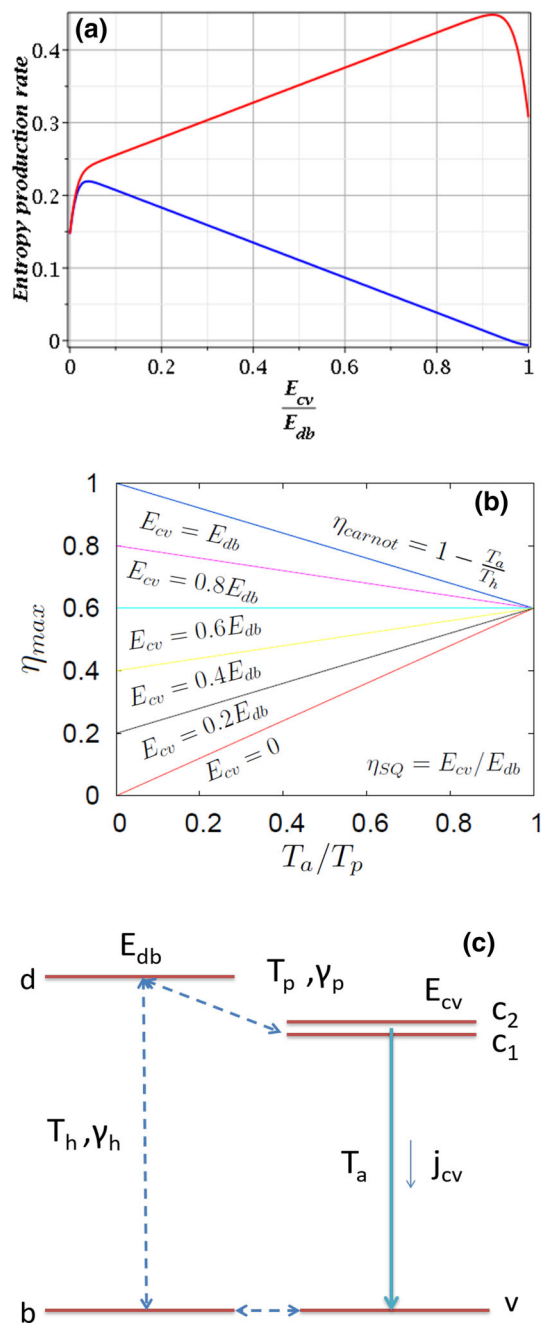


Fig. 2 **a** Comparison of the entropy production rate as a function of E_{cv}/E_{db} as given by Eq. (10) (blue line—can become negative) and Eq. (11) (red line—always positive). **b** Variation of η_{Max} with T_a . For $T_a = 0$, the maximum efficiency is bounded by $\eta_{SQ} = E_{cv}/E_{db} \leq \eta_{Carnot}$, while close to $T_a = T_p$ it is only bounded by η_{Carnot} . **c** Interference of two degenerate $c \leftrightarrow v$ transitions with parallel dipoles

Importantly, Eq. (16) is identical to the efficiency expression obtained from

$$\eta_{Max} = \frac{P}{P_s}, \quad (20)$$

if we identify j_{cv} with Eq. (1),

$$P_s = J_{h \rightarrow S} = \frac{j_s}{e} E_{db}, \quad P = j_{cv} V, \quad (21a)$$

$$eV = E_{cv} + k_B T_a \ln \left(\frac{\rho_{cc}}{\rho_{vv}} \right), \quad (21b)$$

where the ratio of their populations obeys the Fermi-Dirac statistics, $\rho_{cc} = \frac{1}{\exp(\frac{E_{cv} - \mu_c}{k_B T_a}) + 1}$; $\rho_{vv} = \frac{1}{\exp(\frac{E_v - \mu_v}{k_B T_a}) + 1}$. This efficiency bound coincides with the open-circuit limit (Eq. 15), the work term (as in Eq. 2a) being given by Eq. (A11).

Hence, Eq. (20), just like (16) is the genuine efficiency bound for work extractable at steady state, since it takes into account the passivity (generated heat) as a loss contribution in the evaluation of the *net output power*. Alternatively, one has to explicitly account for the loss incurred by the passivity factor in Eqs. (13), (14) for the calculation of power and the efficiency.

7 Boost mechanisms

The case of multiexciton production [16], wherein the quantum efficiency (QE) exceeds 1, can be accounted for in Eq. (20) or (15) by the boost factor $\alpha_{QE} > 1$:

$$j_s \rightarrow \alpha_{QE} j_s, \quad j_{cv} \rightarrow \alpha_{QE} j_{cv}. \quad (22)$$

Since the generated and absorbed power, P and P_s are both boosted by the same factor, η_{Max} is unchanged. In deriving our central result (16) from Eq. (15) we assume that $j_s = j_{cv}$, i.e., current reaches its steady value during the cycle. In case of irreversible tunnelling, it may so happen that $j_{cv} \ll j_s$, i.e., current does not reach a steady value [15]. Then it will strongly affect the efficiency according to Eq. (15).

The same is true in the scenario where, say [1, 2, 5], two degenerate conduction (donor) levels, c_1, c_2 couple to an acceptor (valence) level v (Fig. 2c). The result may be a boost of the heat current $J_{h \rightarrow S}$, $J_{p \rightarrow S}$ and hence a power boost compared to that obtained for level c_1 or c_2 . However, the transition dipoles of the $|c_1\rangle \rightarrow |v\rangle$ and $|c_2\rangle \rightarrow |v\rangle$ transitions must be parallel. Still, the efficiency as opposed to power does not change due to such boost, as in Eq. (20). Hence, the Carnot and SQ bounds remain valid.

8 Conclusions

To conclude, we have put forward a unified thermodynamic analysis of generic, minimal models of solar-powered cyclic processes that can be viewed as quantum heat engines. The resulting general efficiency bound for work production that is consistent with the second law of thermodynamics and allows for passivity and entropy generation has been shown to interpolate

between the Carnot and the Shockley–Queisser bounds. Power boost induced by coherence or multiexcitation generation does not affect the efficiency.

The features analyzed here should allow us to design the conceived solar-pumped schemes that are optimal, both energetically and operationally.

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Author contribution statement

HD and AG have contributed to the research results involved in this paper. MOS has contributed to the formulation of the overall physical picture and Gershon Kurizki has mostly written the article.

A. Appendix: Analysis of the full 4-level scheme

The master equation for the density matrix elements of the system read as follows:

$$\begin{aligned}\dot{\rho}_{dd} &= \gamma_h[\bar{n}_h\rho_{bb} - (\bar{n}_h + 1)\rho_{dd}] + \gamma_p[\bar{n}_p\rho_{cc} - (\bar{n}_p + 1)\rho_{dd}], \\ \dot{\rho}_{cc} &= \gamma_p[(\bar{n}_p + 1)\rho_{dd} - \bar{n}_p\rho_{cc}] + \Gamma[\bar{n}_a\rho_{vv} - (\bar{n}_a + 1)\rho_{cc}], \\ \dot{\rho}_{vv} &= \Gamma[(\bar{n}_a + 1)\rho_{cc} - \bar{n}_a\rho_{vv}] + \gamma_v[\bar{n}_v\rho_{bb} - (\bar{n}_v + 1)\rho_{vv}], \\ \rho_{dd} + \rho_{bb} + \rho_{cc} + \rho_{vv} &= 1,\end{aligned}\quad (\text{A1})$$

where γ_p , γ_h , Γ and γ_v are spontaneous decay rates of the corresponding transitions and $\bar{n}_v = \frac{1}{\exp(\frac{E_{vb}}{k_B T_v}) - 1}$ is the average phonon occupation number for the E_{vb} transition. When E_{vb} becomes zero (Fig. 1c), as discussed in the main text, we note that \bar{n}_v corresponds to very large value, i.e., one may assume $\bar{n}_v \rightarrow \infty$ in this condition (Fig. 3).

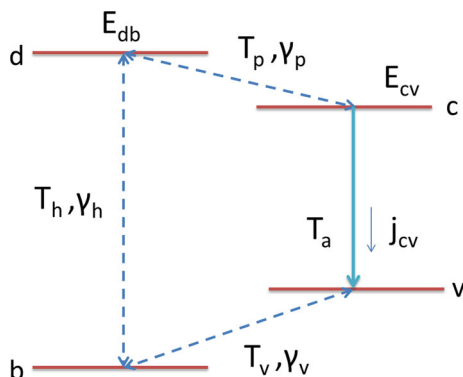


Fig. 3 Generic four-level quantum heat engine (QHE)

Using the relation (1), Eq. (A1) can be simplified as follows:

$$\begin{aligned}\dot{\rho}_{dd} &= \gamma_h[\bar{n}_h\rho_{bb} - (\bar{n}_h + 1)\rho_{dd}] + \gamma_p[\bar{n}_p\rho_{cc} - (\bar{n}_p + 1)\rho_{dd}], \\ \dot{\rho}_{cc} &= \gamma_p[(\bar{n}_p + 1)\rho_{dd} - \bar{n}_p\rho_{cc}] - \frac{j_{cv}}{e}, \\ \dot{\rho}_{vv} &= \frac{j_{cv}}{e} + \gamma_v[\bar{n}_v\rho_{bb} - (\bar{n}_v + 1)\rho_{vv}], \\ \rho_{dd} + \rho_{bb} + \rho_{cc} + \rho_{vv} &= 1.\end{aligned}\quad (\text{A2})$$

The steady state solutions of Eq. (A2) are given by

$$\begin{aligned}\rho_{dd}^{(s)} &= \frac{1 - \left[\frac{1}{\gamma_h \bar{n}_h} \cdot \frac{(2\bar{n}_v + 1)}{(\bar{n}_v + 1)} - \frac{1}{\gamma_p \bar{n}_p} + \frac{1}{\gamma_v (\bar{n}_v + 1)} \right] \frac{j_{cv}}{e}}{3 + \frac{1}{\bar{n}_h} + \frac{1}{\bar{n}_p} + \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_v)}}, \\ \rho_{bb}^{(s)} &= \frac{1 + \frac{1}{\bar{n}_h} + \left[\frac{2 + 1/\bar{n}_p}{\gamma_h \bar{n}_h} - \frac{1 + 1/\bar{n}_h}{\gamma_p \bar{n}_p} - \frac{1 + 1/\bar{n}_h}{\gamma_v (\bar{n}_v + 1)} \right] \frac{j_{cv}}{e}}{3 + \frac{1}{\bar{n}_h} + \frac{1}{\bar{n}_p} + \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_v)}}, \\ \rho_{cc}^{(s)} &= \frac{1 + 1/\bar{n}_p}{3 + \frac{1}{\bar{n}_h} + \frac{1}{\bar{n}_p} + \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_v)}} \left[1 - C \cdot \frac{j_{cv}}{e} \right],\end{aligned}\quad (\text{A3})$$

where,

$$\begin{aligned}C &= \frac{1}{\gamma_h \bar{n}_h} \cdot \frac{(2\bar{n}_v + 1)}{(\bar{n}_v + 1)} + \frac{1}{\gamma_v (\bar{n}_v + 1)} \\ &+ \frac{1}{\gamma_p (1 + \bar{n}_p)} \left[2 + \frac{1}{\bar{n}_h} + \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_v)} \right]\end{aligned}\quad (\text{A4})$$

and

$$\rho_{vv}^{(s)} = \frac{(1 + 1/\bar{n}_v)}{(1 + 1/\bar{n}_v)} \cdot \frac{1 + D \frac{j_{cv}}{e}}{3 + \frac{1}{\bar{n}_h} + \frac{1}{\bar{n}_p} + \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_v)}}, \quad (\text{A5})$$

where

$$D = \frac{2 + 1/\bar{n}_p}{\gamma_h (1 + \bar{n}_h)} + \frac{3 + 1/\bar{n}_h + 1/\bar{n}_p}{\gamma_v \bar{n}_v (1 + 1/\bar{n}_h)} + \frac{1}{\gamma_p \bar{n}_p} \quad (\text{A6})$$

The open-circuit voltage V_{OC} is then obtained for $j_{cv} = 0$ in the form

$$\begin{aligned}eV_{OC} &= \mu_c - \mu_v = E_{cv} + k_B T_a \ln \\ &\times \left[\frac{(1 + 1/\bar{n}_p)(1 + 1/\bar{n}_v)}{(1 + 1/\bar{n}_h)} \right].\end{aligned}\quad (\text{A7})$$

$$\begin{aligned}\frac{eV - eV_{OC}}{k_B T_a} &= \ln \\ &\times \left[\frac{\rho_{cc}^{(s)}}{\rho_{vv}^{(s)}} \cdot \frac{(1 + 1/\bar{n}_h)}{(1 + 1/\bar{n}_p)(1 + 1/\bar{n}_v)} \right].\end{aligned}\quad (\text{A8})$$

Therefore,

$$\exp \left(\frac{eV - eV_{OC}}{k_B T_a} \right) = \frac{1 - C \frac{j_{cv}}{e}}{1 + D \frac{j_{cv}}{e}}. \quad (\text{A9})$$

Or,

$$\frac{j_{cv}}{e} = \frac{1 - \exp \left(\frac{eV - eV_{OC}}{k_B T_a} \right)}{C \left[1 + \frac{D}{C} \exp \left(\frac{eV - eV_{OC}}{k_B T_a} \right) \right]}. \quad (\text{A10})$$

where $\frac{D}{C} = \frac{j_0 e R}{k_B T_a}$, R being the internal resistance of the load.

To recover Eq. (15) we take the limit $\bar{n}_v \rightarrow \infty$ and use the values of \bar{n}_h, \bar{n}_p in Eq. (A7) to obtain

$$eV_{OC} = E_{cv} + k_B T_a \left[\frac{E_{dc}}{k_B T_c} - \frac{E_{db}}{k_B T_h} \right]. \quad (A11)$$

The corresponding heat current expressions are

$$\begin{aligned} J_{h \rightarrow S} &= \gamma_h [\bar{n}_h \rho_{bb} - (\bar{n}_h + 1) \rho_{dd}] E_{ab}, \\ J_{c \rightarrow S} &= \gamma_p [\bar{n}_p \rho_{cc} - (\bar{n}_p + 1) \rho_{dd}] E_{ac} \\ &\quad + \gamma_v [\bar{n}_v \rho_{bb} - (\bar{n}_v + 1) \rho_{vv}] E_{vb}, \\ J_{a \rightarrow S} &= \Gamma [\bar{n}_a \rho_{vv} - (\bar{n}_a + 1) \rho_{cc}] E_{cv}. \end{aligned} \quad (A12)$$

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