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On the thermodynamics of the difference between energy transfer rate and heat engine efficiency

H. Dong[1], A. Ghosh[2], M. B. Kim[3], S.-W. Li[4], A. A. Svidzinsky[3], Z. Zhang[3], G. Kurizki[5], and M. O. Scully[3,6,7,a]

[1] Graduate School of China Academy of Engineering Physics, No. 10 Xibeiwang East Road, Haidian District, Beijing 100193, China
[2] Department of Physics, Shanghai University, Baoshan District, Shanghai 200444, China
[3] Institute for Quantum Science and Engineering, Texas A&M University, College Station, TX, USA
[4] Center for Quantum Technology Research, School of Physics, Beijing Institute of Technology, Beijing 100081, China
[5] Weizmann Institute of Science, 76100 Rehovot, Israel
[6] Princeton University, Princeton, NJ, USA
[7] Baylor University, Waco, TX, USA

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Abstract We study the difference between the energy transfer rate and the engine efficiency with a microscopic model, widely used in the theoretical description of solar cells, as well as in light-harvesting systems. We show no violation of the second law of thermodynamics by correctly assessing the useful output work, even with the simple model treating the later work conversion as a simple "sink".

1 Introduction

Quantum thermodynamics is a subtle blend of quantum and classical thermodynamics physics. On the one hand, the second law of thermodynamics is generally accepted: any amount of work can be turned into heat, but heat cannot be totally converted to work (Kelvin-Planck statement). However, quantum mechanics can point the way to bypass the restriction in some way. For example, Ramsey showed that with the existence of negative temperature, the Kelvin-Planck statement has to be modified [1].

It is therefore important to carefully analyze problems of quantum and classical thermodynamics interpretation to properly understand the thermal and quantum physics. Recently, an interesting study showed that a possible violation of the second law of thermodynamics exists in a widely used model of natural light-harvesting and solar cell [2]. However, we find that, such seeming violation roots from some subtle difference of two concepts, the total energy output and the useful work output. It is known that the energy output is often accompanied by entropy output, therefore, not all the output energy can be used for work. Only part of the output energy can be used to produce chemicals or perform work. Based on the solar cell model, we give the right prescription for calculating the useful output work, which just has the familiar form of free energy, and satisfies the requirement of the second law.

An intriguing problem is how to improve the current technology to harvest solar energy more efficiently and quickly [3–5]. Such efforts to understand the natural light-harvesting have led to the discovery of long-lived coherence in natural light-harvesting systems [6–8], such as the Fenna-Matthews-Olson (FMO) complex [9] in green sulfur bacteria, bacterial reaction center [10–13], and LHCII in spinach [14]. These discoveries have boosted investigations to understand microscopic model of biological light-harvesting systems [15].

It is suggested that the structures, preserving such coherence in light-harvesting systems may inspire new designs of light conversion devices [4,16]. For the purpose of understanding the advantage of these structures in natural light-harvesting systems, a quantity to characterize the improvement is necessary. From a thermodynamic perspective [17,18], both types of sunlight conversions can be uniformly treated as heat engines which utilize the temperature difference between two reservoirs— the Sun and the Earth in this case. For the heat engine, the efficiency and the output power are two quantities to characterize its effectiveness. It was shown that the output power, energy output per unit time, can be significantly improved via a noise induced coherence [17,19,20].

The paper is organized as follows. In Sect. 2, we analyze the energy flux in the light-harvesting model. In Sect. 3, we discuss efficiency of an electron-current heat engine based on the useful output work, and show that it well satisfies the requirement of the second law.

[a] e-mail: scully@tamu.edu (corresponding author)

2 Energy flux in light-harvesting model

In light-harvesting systems, sunlight is mainly captured by antenna complexes. The captured energy is subsequently transferred to reaction centers, where the charge separation process produces electrons for later chemical reactions [21]. This process of energy capture and transfer can be simply described by a donor-acceptor model [2,18], illustrated in Fig. 1. A donor molecule absorbs one photon from the Sun, resulting in a transition of its state from $|a\rangle$ to $|b\rangle$. The absorbed energy is then transferred to the acceptor, with energy levels $|c\rangle$ and $|v\rangle$. Such transfer is achieved through the interaction with surrounding proteins environment (denoted as blue lines) with temperature T_c. Then energy is directed to the outside agent to synthesize chemicals. Such model was firstly used in studying the efficiency of solar cells [17,20].

The evolution of this system can be described by the following master equation

$$\frac{d\rho_S}{dt} = -i\left[H_S, \rho_S(t)\right] + \left(\mathcal{L}_h + \mathcal{L}_c + \mathcal{L}_l\right)\rho_S(t), \qquad (1)$$

where H_S is the Hamiltonian for the system. Here, $\mathcal{L}_h$, $\mathcal{L}_c$ and $\mathcal{L}_l$ are the Liouville operators for the interaction of our system with a hot bath (the Sun), a cold bath (the Earth environment), and an output circuit respectively.

The internal energy of the engine is defined as $E_S(t) = \mathrm{tr}\left[\rho_S(t)H_S\right]$, by which the rate of energy change is [18,22,23],

$$\frac{dE_S(t)}{dt} \equiv \mathrm{tr}\left[\frac{d\rho_S}{dt}H_S\right]. \qquad (2)$$

The energy change of the system (engine) is caused by exchanging energy, i.e., heat or work, with baths and output circuits, namely $dE_S(t)/dt = \mathcal{J}_{h\to S} + \mathcal{J}_{c\to S} + \mathcal{J}_{l\to S}$. Here $\mathcal{J}_{h\to S}$, $\mathcal{J}_{c\to S}$, and $\mathcal{J}_{l\to S}$ are energy flows from the hot bath, the cold bath, and the output circuit. Plugging Eq. (1) into Eq. (2), we sort the energy flows

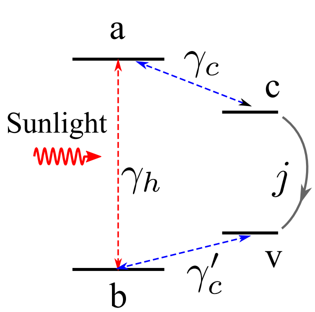

Fig. 1 Scheme of a donor-acceptor/solar-cell model. The red lines show the coupling to the hot bath, while blue lines show the coupling to the cold bath. The output is denoted as an arc, and the incident sunlight is marked as a wavy line

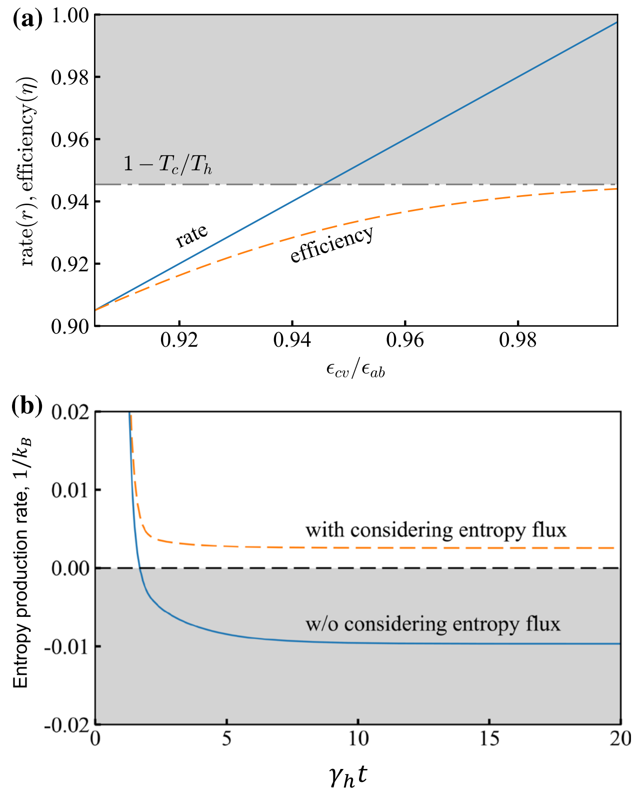

Fig. 2 Efficiency (**a**) and entropy production rates (**b**) in donor-acceptor/solar-cell model. **a** Energy transfer rate (solid line) and heat engine efficiency (dashed line) as a function of ratio $\epsilon_{cv}/\epsilon_{ab}$. The dash-dotted line shows the Carnot efficiency $\eta_{\mathrm{Carnot}} = 1 - T_c/T_h$. The shaded area indicates the second law violation region. In simulations we take $T_h = 5500\,\mathrm{K}$, $T_c = 300\,K$, $\epsilon_b = 0$, $\epsilon_a = 0.7\,\mathrm{eV}$ and $\epsilon_v = 0.1\,\mathrm{eV}$. **b** Entropy production rates with and without including the entropy flux into the load as a function of time t. Initially the system is in the ground state $|b\rangle$

from each sources or output circuit to the system as

$$\mathcal{J}_{x\to S} = \mathrm{tr}\big[\mathcal{L}_x[\rho_S]H_S\big], \qquad x = h, c, l.$$

Entropy fluxes accompany these energy flows. To derive the entropy fluxes, we define the entropy of our system via von Neumann formula as $S_S = -k_{\mathrm{B}}\mathrm{tr}\left[\rho_S \ln \rho_S\right]$. The entropy change can be in turn written as

$$\frac{dS_S(t)}{dt} = -k_{\mathrm{B}}\mathrm{tr}\left[\frac{d\rho_S}{dt}\ln \rho_S\right].$$

We have simplified this equation by noticing the normalization condition $\mathrm{Tr}\rho_S(t) = 1$. Similarly, we define the entropy fluxes from the hot and cold bath, and the output circuit to the engine

$$\mathcal{S}_{x\to S} := -k_{\mathrm{B}}\mathrm{tr}[\mathcal{L}_x[\rho_S]\ln \rho_S], \qquad x = h, c, l.$$

It is reasonable that heat baths have entropy fluxes into and out of the heat engine. However, the entropy directed to the output agent is not included in the current model of the light-harvesting process. We will show how these entropy fluxes help us to save the second law of thermodynamics.

The components of the master equation read

$$\frac{d}{dt}\rho_{aa} = -\gamma_h[(n_h+1)\,\rho_{aa} - n_h\rho_{bb}] - \gamma_c\left[\left(n_{ac}^{(c)}+1\right)\rho_{aa} - n_{ac}^{(c)}\rho_{cc}\right], \tag{3}$$

$$\frac{d}{dt}\rho_{cc} = \gamma_c[(n_{ac}^{(c)}+1)\rho_{aa} - n_{ac}^{(c)}\rho_{cc}] - \Gamma\rho_{cc}, \tag{4}$$

$$\frac{d}{dt}\rho_{vv} = \Gamma\rho_{cc} - \gamma_c'\left[\left(n_{vb}^{(c)}+1\right)\rho_{vv} - n_{vb}^{(c)}\rho_{bb}\right], \tag{5}$$

$$1 = \rho_{aa} + \rho_{bb} + \rho_{cc} + \rho_{vv}, \tag{6}$$

where $n_h = 1/(\exp[\epsilon_{ab}/k_B T_h] - 1)$, $n_{ac}^{(c)} = 1/(\exp[\epsilon_{ac}/k_B T_c] - 1)$ and $n_{vb}^{(c)} = 1/(\exp[\epsilon_{vb}/k_B T_c] - 1)$ are the average number of photons with the energies $\epsilon_{ab} \equiv \epsilon_a - \epsilon_b$, $\epsilon_{av} \equiv \epsilon_a - \epsilon_v$, and $\epsilon_{vb} \equiv \epsilon_v - \epsilon_b$ respectively. Here, γ_h and $\gamma_c(\gamma_c')$ are the dissipation rates corresponding to the coupling to the hot and the cold baths, and Γ is the rate of energy flow into outside agent.

Based on the above definition of the energy fluxes $\mathcal{J}_{h\to S}$, $\mathcal{J}_{c\to S}$, and $\mathcal{J}_{l\to S}$, using the evolution equations, we obtain

$$\begin{aligned}\mathcal{J}_{h\to S} &= -\gamma_h[(n_h+1)\rho_{aa} - n_h\rho_{bb}]\epsilon_{ab},\\ \mathcal{J}_{c\to S} &= -\gamma_c[(n_{ac}^{(c)}+1)\rho_{aa} - n_{ac}^{(c)}\rho_{cc}]\epsilon_{ac} - \gamma_c'[(n_{vb}^{(c)}+1)\rho_{vv} - n_{vb}^{(c)}\rho_{bb}]\epsilon_{vb},\\ \mathcal{J}_{l\to S} &= -\Gamma\rho_{cc}\epsilon_{cv}.\end{aligned}$$

Note that when the system is operating as a usual heat engine, the energy flows through the system from the hot-temperature thermal bath to the colder environment. Then, the signs of the energy flow are $\mathcal{J}_{h\to S} > 0$, $\mathcal{J}_{c\to S} < 0$, and $\mathcal{J}_{l\to S} < 0$.

Using energy conservation, we can obtain the energy flux from the system to the environment as opposite to the energy flux into the system

$$\mathcal{J}_{S\to h} = -\mathcal{J}_{h\to S}, \quad \mathcal{J}_{S\to c} = -\mathcal{J}_{c\to S}, \quad \text{and} \quad \mathcal{J}_{S\to l} = -\mathcal{J}_{l\to S}.$$

However, there is no such a relation for the entropy flux since the entropy can be produced in an irreversible process.

3 Output energy and useful work

In the steady state ($d\rho_{ii}/dt = 0$, $i = a, b, c, v$), adding Eq. (3) to Eq. (4) gives the following simple relation

$$-\gamma_h[(n_h+1)\,\rho_{aa} - n_h\rho_{bb}] = \Gamma\rho_{cc}. \tag{7}$$

Note that the two sides of the above relation are just the energy fluxes $\mathcal{J}_{h\to S}$ and $\mathcal{J}_{l\to S}$ found in the last section. Therefore, we obtain

$$r = \frac{|\mathcal{J}_{l\to S}|}{|\mathcal{J}_{h\to S}|} = \frac{\epsilon_{cv}}{\epsilon_{ab}}.$$

This is the ratio between the output energy flow ($\mathcal{J}_{S\to l}$) and the input energy flow ($\mathcal{J}_{h\to S}$) from the Sun. We will call it the energy transfer ratio.

This energy transfer ratio is independent of the temperature difference between the hot and the cold baths. It was pointed out that this independence of the temperature difference might lead to a violation of the second law of thermodynamics [2]. In Fig. 2a, we plot the ratio r as a function of $\epsilon_{cv}/\epsilon_{ab}$ as a solid line. The curve for the Carnot efficiency $\eta_{\text{Carnot}} = 1 - T_c/T_h$ is shown as a dash-dot line. The gray shaded area is the second law violation zone. The ratio r indicates a "violation" of the second law of thermodynamics in the shaded area $\epsilon_{cv}/\epsilon_{ab} > 1 - T_c/T_h$.

However, it is well known that the energy flow towards the output circuit can not be completely extracted as a work. The concept of passivity is proposed to evaluate the maximum work extracted from a system at a particular state without any other reservoirs. The passivity has been applied to various heat engines to study the corresponding efficiency [24–28]. For our case, the output is an energy flow accompanying the entropy flux. The key is to evaluate the amount of work in this energy flow.

For the case of a solar cell, the work can be directly delivered to the output electrical circuit as electric power, which can be calculated via the output voltage V and the electric current I. Since two energy states, $|c\rangle$ and $|v\rangle$, are considered in the energy bands of the grand canonical ensemble, the voltage is defined as the chemical potential difference $eV = \mu_c - \mu_v$. The chemical potentials are given by the following equations

$$\rho_{cc} = \exp[-(\epsilon_c - \mu_c)/k_B T_c], \tag{8}$$

$$\rho_{vv} = \exp[-(\epsilon_v - \mu_v)/k_B T_c]. \tag{9}$$

From Eqs. (8), (9) the voltage can be explicitly written as

$$eV = \epsilon_c - \epsilon_v + k_B T_c \ln\frac{\rho_{cc}}{\rho_{vv}}. \tag{10}$$

The current to the output circuit is $I = e\Gamma\rho_{cc}$. The output power reads

$$\mathcal{P} = \epsilon_{cv}\Gamma\rho_{cc} + k_B T_c\Gamma\rho_{cc}\ln\frac{\rho_{cc}}{\rho_{vv}}. \tag{11}$$

Under the condition of having no population inversion, $\rho_{cc} < \rho_{vv}$, the output power $\mathcal{P}$ is smaller than the energy flow out to the circuit. The efficiency of the engine is defined as $\eta \equiv \mathcal{P}/\mathcal{J}_{h\to S}$. At steady state, the efficiency is

$$\eta = \frac{1}{\epsilon_{ab}}\left(\epsilon_{cv} + k_B T_c \ln\frac{\rho_{cc}}{\rho_{vv}}\right).$$

In Fig. 2a, we plot the efficiency η as a function of $\epsilon_{cv}/\epsilon_{ab}$ as a dashed line. The curve for the efficiency shows a smaller amount of energy extracted to the outside circuit than the total energy flow, and the efficiency is smaller than the Carnot efficiency.

Now the question is: what is the physical meaning of the additional term $k_B T_c \Gamma \rho_{cc} \ln(\rho_{cc}/\rho_{vv})$ in Eq. (11) for the output power? Here we will show that this term corresponds to a heat flow related to the entropy flux. Before proceeding, we note that the temperature of the load is not specified, even though Eq. (11) might suggest that the temperature of the load is T_c.

Analogously to the previous energy flow relations, the entropy change of the system, $\dot{S}_S$, leads to the entropy flux exchange with with the hot and the cold bath, and the output circuit, $\mathcal{S}_{x\to S} = -k_B \text{tr}[\mathcal{L}_x[\rho_S] \ln \rho_S]$ for $x = h, c, l$. Combining these expressions with the equations of motion, the entropy flux output to the outside circuit yields

$$\mathcal{S}_{S\to h} + \mathcal{S}_{h\to S} \geq 0, \qquad \mathcal{S}_{S\to c} + \mathcal{S}_{c\to S} \geq 0,$$
$$\mathcal{S}_{S\to l} + \mathcal{S}_{l\to S} \geq 0.$$

The relation for the entropy flux between the system and the load gives

$$\mathcal{S}_{S\to l} \geq -\mathcal{S}_{l\to S} = k_B \Gamma \rho_{cc} \ln \frac{\rho_{cc}}{\rho_{vv}}. \qquad (12)$$

Thus, with this entropy flux, we can say that the entropy is eventually dumped into the load, and more entropy might be generated during this irreversible process. And, it implies that only the portion of the energy flow without entropy can be treated as work.

The maximum useful work W that can be done by the system when the electron undergoes a 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

$$W = eV = E_{cv} - T_c \Delta S_{S\to l},$$

where $\Delta S_{S\to l}$ (as defined above) is the change in the entropy of the system when the electron undergoes the $c \to v$ transition. When $|c\rangle$ and $|v\rangle$ correspond to steady states, the above W can be easily identified with the change in the Helmholtz free energy. Note that $\Delta S_{S\to l}$ 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. One should note that the above equation is equivalent to the output power discussed in the last section [see Eqs. (10, 12)].

4 Entropy production rate

Another way of looking into the second law of thermodynamics is the entropy production rate, which is always positive. A peculiar entropy production rate was defined in Ref. [2] as

$$\sigma \equiv \dot{S}_S - \frac{\mathcal{J}_{h\to S}}{T_h} - \frac{\mathcal{J}_{c\to S}}{T_c}, \qquad (13)$$

where $\dot{S}_S$ is the entropy change rate of the system. The corresponding curve for this entropy production rate is shown as a solid line in Fig. 2b. At steady state, the curve reveals a negative entropy production rate.

However, the definition of the entropy production rate (13) has obviously neglected the entropy flux from the heat engine to the outside agent, which seemingly violates the Planck's statement of the Second Law: "*Every process occurring in nature... the sum of the entropies of all bodies taking part in the process is increased* " [29]. With this observation, we define the entropy production rate as

$$\sigma' \equiv \dot{S}_S - \frac{\mathcal{J}_{h\to S}}{T_h} - \frac{\mathcal{J}_{c\to S}}{T_c} + \mathcal{S}_{S\to l}.$$

This new definition of the entropy production rate σ' is plotted in Fig. 2b as a dashed line, which is always positive [30].

5 Summary

In summary, we have shown that the efficiency of the simple donor-acceptor/solar-cell model is bound by the Carnot efficiency, and clearly shows no violation of the second law of thermodynamics. We emphasize the difference between the energy transfer rate and the heat engine efficiency in the present model. The energy transfer rate was evaluated in many previous investigations of natural light-harvesting systems [31]. However, such a rate does not reveal the amount of the transferred energy which can be converted into useful work.

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