How Much is the Efficiency of Solar Cells Enhanced by Quantum Coherence?

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We study how much the efficiency of a solar cell as a quantum heat engine could be enhanced by quantum coherence. In contrast to the conventional approach that a quantum heat engine is in thermal equilibrium with both hot and cold reservoirs, we propose a new description that the quantum heat engine is in the cold reservoir and the thermal radiation from the hot reservoir is described by the pumping term in the master equation. This pumping term solves the problem of the incorrect mean photon number of the hot reservoir assumed by the previous studies. By solving the master equation, we obtain the current-voltage and the power-voltage curves of the photocell for different pumping rates. We find that, as the photon flux increases, the power output of the photocell increases linearly at first and then becomes saturated, but the efficiency decreases rapidly. It is demonstrated that while the power output is enhanced significantly by the quantum coherence via the dark state of the coupled donors, the improvement of the efficiency is not significant.

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Solar cells and photosynthesis, which convert sunlight into electrical and chemical energies, respectively, may be regarded as heat engines. The maximum efficiency of a heat engine operating between hot and cold reservoirs is known as the Carnot efficiency, derived from the second law of thermodynamics. For a quantum heat engine, Scovil and Schulz-DuBois considered a three-level maser in thermal contact with two heat reservoirs, and showed its ultimate efficiency is that of a Carnot engine [1]. Shockley and Queisser obtained the upper limit of efficiency of a single p-n junction solar cell, based on the assumption that electron-hole pairs recombine only through the radiative process, i.e., the principle of the detailed balance [2]. The Shockley-Queisser limit, however, is far below the Carnot efficiency because of only one electron-hole pair generation per photon with energy larger than the band gap of the semiconductor generates.

Recent studies have shown that quantum effects could play a key role in photosynthesis and solar cells. Engel and his co-workers observed the long-lived quantum coherence in exciton dynamics in the Fenna-Matthews-Olsen complex, using 2-dimensional electronic spectroscopy [3]. Following experimental and theoretical studies suggest that this quantum beat may be due to the interplay of electronic and vibronic quantum dynamics. Scully and his colleagues showed theoretically that quantum coherence could enhance the efficiency of a solar cell and a photosynthetic reaction center [4, 5]. It has been argued that the quantum coherence could break the detailed balance, and thus the Shockley-Queisser limit of the efficiency of solar cells.

Inspired by Scully et al.’s work, Creatore et al. [6] proposed a biologically inspired photocell model enhanced by a delocalized dark quantum state of two dipole-dipole coupled donors. Zhang et al. [4] showed that the delocalized dark state of three coupled donors could enhance more the efficiency of a photocell. Recently, Fruchtman et al. [11] showed that a photocell with asymmetric pair of coupled chromophores could outperform those with the symmetric dimer or with a pair of independent molecules.

While theoretical studies on photocells mentioned above predict promising enhancement of the efficiency of a quantum heat engine, there is controversy, especially, raised by Kirk [12, 14]. The claim of the role of quantum coherence in enhancing the efficiency needs to be more complete in the following sense. First, photocells as a quantum heat engine are assumed to be in thermal equilibrium with hot and cold reservoirs simultaneously. This assumption may give rise to a question on the temperature of a photocell. Second, the average photon number of the Sun with a temperature of 6000 K at the energy gap of donors was incorrectly used in the master equations in previous studies. Finally, while the previous studies have shown the power enhancement by quantum effects, they tells neither how much efficiency is enhanced nor whether the Shockley-Queisser limit is surpassed.

In the paper, we present a realistic model of a photocell which is in thermal contact only with the cold reservoir. The pumping term in a master equation is introduced in order to take into account the photon flux from the hot reservoir. This resolves the issue of the incorrect mean photon number of the hot reservoir assumed by the previous studies, and makes it possible to calculate the efficiency. The power output of the photocell is obtained as a function of the strength of the pumping term, i.e., the photon flux. We show that the power increases linearly at first but becomes saturated as the pumping strength increases. We obtain the efficiency as a function of pumping strength and demonstrate that quantum coherence could enhance the efficiency, but not much.

Solar Cell with Donor-Acceptor.— Let us start with a simple photovoltaic model, a four-level quantum sys-
tem composed of a donor and an acceptor, as shown in Figs. 1 (a) and (b). We present the issue of the previous photocell models and solve it by introducing the pumping term in our model. Fig. 1 (a) depicts a photocell model of previous studies that is in the thermal equilibrium with both hot and cold reservoirs at the same time. The total Hamiltonian is written formally as

$$H = H_S + H_H + H_C + H_{SH} + H_{SC},$$  \hspace{1cm} (1)

where $H_S$ is the Hamiltonian of the photocell with donor and acceptor, and $H_H$ ($H_C$) is the Hamiltonian of the hot (cold) reservoir represented by the collection of the harmonic oscillators. Typically, it is assumed that the interactions, $H_{SH}$ and $H_{SC}$, between the system and the reservoirs are assumed to be time-independent. Using the Born and the Markov approximations, one can obtain the master equation for the system dynamics.

As shown in the previous studies \[^2\text{11}\], the probabilities $P_i$ of occupation of energy levels $E_i$ obey the Pauli master equations

$$\dot{P}_0 = \gamma_{01} [n_{01}^h + 1] P_1 - n_{01}^h P_0 + \chi \Gamma P_\alpha$$

$$+ \gamma_{0\beta} [n_{0\beta}^h + 1] P_\beta - n_{0\beta}^h P_0,$$  \hspace{1cm} (2a)

$$\dot{P}_1 = \gamma_{01} [n_{01}^h P_0 - (n_{01}^h + 1) P_1]$$

$$+ \gamma_{1\alpha} [n_{1\alpha}^c P_\alpha - (n_{1\alpha}^c + 1) P_1],$$  \hspace{1cm} (2b)

$$\dot{P}_\alpha = \gamma_{\alpha 1} [n_{\alpha 1}^c + 1] P_1 - n_{\alpha 1}^c P_\alpha - (1 + \chi) \Gamma P_\alpha,$$  \hspace{1cm} (2c)

$$\dot{P}_\beta = \gamma_{\beta 0} [n_{\beta 0}^c P_0 - (n_{\beta 0}^c + 1) P_\beta] + \Gamma P_\beta.$$  \hspace{1cm} (2d)

Here $\gamma_{ij}$ are the transition rates between level $E_i$ to level $E_j$. The mean photon number $n_{ij}^h$ ($n_{ij}^c$) of the hot (cold) reservoir at temperature $T_h$ ($T_c$) for a given frequency $\Delta E_{ij} = E_j - E_i$ is written as

$$n_{ij}^h = \frac{1}{e^{\Delta E_{ij}/k_B T_h} - 1}. \hspace{1cm} (3)$$

The parameters are taken as follows: $E_1 - E_0 = 1.8 \text{ eV}$, $E_1 - E_\alpha = E_\beta - E_0 = 0.2 \text{ eV}$, $h\gamma_{01} = 1.24 \mu\text{eV}$, $h\gamma_{1\alpha} = 12 \text{ meV}$, and $h\gamma_{0\beta} = 24 \text{ meV} \[^2\text{11}\]$. These imply $1/\gamma_{01} \simeq 0.5 \text{ ns}$, $1/\gamma_{1\alpha} \simeq 0.55 \text{ fs}$, $1/\gamma_{0\beta} \simeq 0.26 \text{ fs}$, and $\chi = 0$. So, the typical time to reach the steady state is the order of femtosecond. The temperatures of the hot and cold reservoirs are $T_h = 6000 \text{ K}$ and $T_c = 300 \text{ K}$, respectively. If the parameters are plugged into Eq. (3), the mean photon number of the hot reservoir at energy $\Delta E_{01} = 1.8 \text{ eV}$ is given by $n_{01}^h \approx 0.0317$, and the mean photon number of the cold reservoir at energy $\Delta E_{1\alpha} = \Delta E_{1\beta} = 0.2 \text{ eV}$ by $n_{1\alpha}^c = n_{1\beta}^c \approx 4.368 \times 10^{-4} \[^2\text{12}\]$. However, the previous papers earlier \[^2\text{11}\] assumed $n_{01}^h = 60000$ that does not coincide with the value given by Eq. (3).

In order to solve the pitfall of the previous studies depicted in Fig. 1 (a), we propose a new photocell model as shown in Fig. 1 (b). The donor of the new photocell is assumed to be in thermal equilibrium only with the cold reservoir, but not with the hot reservoir. The photon flux from the hot reservoir is described by the pumping term \[^2\text{10}\]. So the strength of the pumping term may correspond to the solar irradiance incident on the photocell. It is straightforward to obtain the Pauli master equations with the pumping term for the population dynamics of the new photocell model

$$\dot{P}_0 = \gamma_{01} [n_{01}^c + 1] P_1 - n_{01}^c P_0 + \chi \Gamma P_\alpha$$

$$+ \gamma_{0\beta} [n_{0\beta}^c + 1] P_\beta - n_{0\beta}^c P_0 + W_p (P_0 - P_\beta),$$  \hspace{1cm} (4a)

$$\dot{P}_1 = \gamma_{01} [n_{01}^c P_0 - (n_{01}^c + 1) P_1]$$

$$+ \gamma_{1\alpha} [n_{1\alpha}^c P_\alpha - (n_{1\alpha}^c + 1) P_1] + W_p (P_1 - P_\beta),$$  \hspace{1cm} (4b)

$$\dot{P}_\alpha = \gamma_{\alpha 1} [n_{\alpha 1}^c + 1] P_1 - n_{\alpha 1}^c P_\alpha - (1 + \chi) \Gamma P_\alpha,$$  \hspace{1cm} (4c)

$$\dot{P}_\beta = \gamma_{\beta 0} [n_{\beta 0}^c P_0 - (n_{\beta 0}^c + 1) P_\beta] + \Gamma P_\beta.$$  \hspace{1cm} (4d)

Note that the mean photon number $n_{01}^h$ of the hot reservoir in Eq. (2) is replaced by $n_{01}^c$ of the cold reservoir and the pumping term $W_p$ in Eq. (4). The mean photon number $n_{01}^c = 60,000$ of the previous studies \[^2\text{11}\] corresponds to $W_p/\gamma_{01} \simeq 60,000$ and $W_p \approx 1.1 \times 10^{15} \text{ s}^{-1}$. It is instructive to compare this pumping rate with the number of photons incident per unit area per unit time for the black-body radiation of the Sun at temperature $T_s = 6000 \text{ K}$, using the Planck distribution. The number of photons with energy greater than the energy gap $E_g = h\nu_g$ absorbed by the donor per unit area per unit

![Diagram of hot and cold reservoirs](image-url)
time is given by

$$Q_s(\nu, T_s) = \frac{2\pi}{c^2} \int_{\nu_\gamma}^{\infty} \frac{\nu^2}{e^{\hbar\nu/k_BT_s} - 1} d\nu. \quad (5)$$

For $E_g = 1.8 \text{ eV}$, one obtains $Q_s \approx 9.0 \times 10^{25} \text{ m}^{-2} \text{ s}^{-1}$. So the pumping rate $W_p = 10^{12} \text{ s}^{-1}$ corresponds to the photon flux incident on a photocell with area $0.1 \mu\text{m}^2$.

Eq. (1) is solved numerically using the Runge-Kutta method. After the populations reach the steady state, the current is calculated as $I = eT_s P$, and the voltage as $V = E_\alpha - E_\beta + k_B T s \ln(P_{\alpha}/P_{\beta})$. By changing the resistance $\Gamma$ of the external load from zero to infinity, one obtains the current-voltage curve of the photocell for various pumping rates, as shown in Fig.2. The magnitude of current $I$ is readily estimated as follows. The generation rate of the excited electrons is proportional to the pumping rate, for example $W_p = 10^{12} \text{ s}^{-1}$. The transfer rate of the excited electrons to the acceptor is fast, i.e., the order of femtosecond. Thus, the current is just given by the product of electron charge and the generation rate, $I \sim 1.6 \times 10^{-19} \text{ C} \times 10^{12} \text{ s}^{-1} = 0.16 \mu\text{A}$, i.e., the order of microampere.

![Figure 2. (a) Current $I$ and (b) power $P$ are plotted as a function of voltage $V$ for different pumping rates $W_p$.](image)

We investigate how the efficiency and the maximum power change as a function of the pumping rate. The efficiency $\eta$ of the photocell is calculated as

$$\eta = \frac{P_{\text{out}}}{P_m} = \frac{P_m \left[\mu\text{W}\right]}{1.8 \left[\text{eV}\right] \cdot W_p \left[\text{s}^{-1}\right]} . \quad (6)$$

It would be expected that the more power the photocell generates, the higher solar irradiance it receives. However, as shown in Fig.3 the maximum power increases linearly at the beginning but becomes saturated above a certain value of the pumping rate. This implies that there is a bottleneck in population dynamics. A saturation curve like Fig.3 can be found in photosynthesis, which is well known as the photosynthesis-irradiance curve [17, 19]. Note that the maximum power as a function of pumping rate $W_p$ can be fitted by $P(W_p) = a \cdot W_p/(W_p + b)$ with $a = 1.1$ and $b = 7$. We find that the efficiency of the photocell decreases as the pumping rate $W_p$ increases.

![Figure 3. Efficiency (blue solid line) and the maximum power $P_m$ (red dashed line) are plotted as a function of the pumping rate $W_p$.](image)

**Photocell with coupled donors and an acceptor.** — Let us turn to the main question how much the efficiency of a photocell is enhanced by quantum coherence. Similar to the previous studies [8, 9], we consider the photocell model composed of two coupled donors and an acceptor, as shown in Fig.4. Unlike the previous studies, the photocell is in thermal equilibrium only with the cold reservoir. The coupled donors form the bright state $|2\rangle$ and the dark state $|1\rangle$.

![Figure 4. A photocell with coupled donors and an acceptor is in thermal equilibrium only with the cold reservoir. The coupled donors form the bright state $|2\rangle$ and the dark state $|1\rangle$.](image)
dynamics for occupation probabilities of energy level $E_i$ is readily given by the Pauli master equation

$$\dot{P}_0 = \gamma_{01} \left[ (1 + n_{01}^c) P_1 - n_{01}^c P_0 \right] + \chi \Gamma P_\alpha,$$

where $\chi$, $\Gamma$, and $P_\alpha$ are given by Eqs. (7a) and (7b).

We solve Eq. (7) with the parameters $\gamma_{ij}$ given by Refs. [3] [4]. We obtain the current-voltage curve and the power-voltage curve for different pumping rates and for photocells with uncoupled and coupled donors to see the effect of quantum coherence, as shown in Fig. 5 It is interesting that at low pumping rate $W_p = 10^{12}$ s$^{-1}$, the short-circuit current and the power are not enhanced by the quantum coherence. However, at high pumping rate $W_p = 10^{15}$ s$^{-1}$, the quantum coherence gives rise to the strong enhancement of the short-circuit current and the power, agreeing with the previous studies [5–11]. Fig. 6 depicts the maximum power $P_m$ and the efficiency as a function of pumping rate $W_p$ for coupled and uncoupled donors. For both uncoupled and coupled donors, the maximum power $P_m$ increases at first and becomes saturated as the pumping rate increases, but the efficiency decreases. The photocell with coupled donors generates more power than that with uncoupled donors as the pumping rate increases, but the enhancement in efficiency due to the quantum coherence is not the case. In contrast to the claim of the previous studies [5–11], the enhancement of the efficiency due to the quantum coherence, via dark states or noise-induced quantum coherence, is very small at $W_p = 10^{15}$ s$^{-1}$ which corresponds to $n_{02}^c = 60,000$.

In conclusion, we proposed a new photocell model where the system is in thermal equilibrium only with the cold reservoir and the photon flux from the hot reservoir is described by the pumping term in the master equation. The pumping term resolves the problem of the incorrect mean photon number of the hot reservoir used by the previous studies. The maximum power and the efficiency were obtained as a function of the pumping rate. It is found that as the pumping rate increases, the power increases linearly at first but becomes saturated, and the efficiency decreases rapidly. It is shown that the quantum coherence via the dark state of the coupled donors clearly enhance the power significantly, but the efficiency tiny. Further study is needed to see whether quantum coherence could enhance the efficiency significantly and break the Shockley-Queisser limit of a single-junction solar cell.
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