# Quantum Photocell: Using Quantum Coherence to Reduce Radiative Recombination and Increase Efficiency

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The fundamental limit to photovoltaic efficiency is widely thought to be radiative recombination which balances radiative absorption. We here show that it is possible to break detailed balance via quantum coherence, as in the case of lasing without inversion and the photo-Carnot quantum heat engine. This yields, in principle, a quantum limit to photovoltaic operation which can exceed the classical one. The present work is in complete accord with the laws of thermodynamics.

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The efficiency of photovoltaic energy conversion [1] is an important aspect of solar cell or photodetector operation. The early *p*-*n* junction Si solar cells had an efficiency of around 5%; the (empirical) limit at that time was thought to be 20% [2]. Half a decade later, Shockley and Quiesser [3] showed that the limit was more correctly attributed to the fact that electron-hole pairs are often lost due to radiative recombination before they can contribute to useful work.

Here we analyze a toy photocell illuminated by a monochromatic slice of the solar spectrum to show how we can mitigate radiative recombination and enhance efficiency via quantum coherence. For simplicity, we will focus on a *pn* photodiode in a single mode cavity or photon band gap material [4].

We begin by briefly reviewing the underlying physics germane to the present Letter, namely, (1) lasing without inversion (LWI) and (2) photocell operation. Then we show how to combine quantum coherence and cavity quantum electrodynamics to, in principle, make a quantum dot photodiode in a cavity more efficient [4].

We recall that electrons excited to the conduction band by photons having energy greater than the energy gap between the conduction and valence bands will be thermalized by multiple phonon emission [1] as they settle to the bottom of the band. The resulting energy conversion efficiency, known as the Shockley-Quiesser recombination limit, is found [3] to be over 30%.

Clearly, the energy loss due to crystal vibrations is not a fundamental limit. It can be overcome [1] by separation of the solar spectrum into narrow frequency intervals, and then directing each frequency ($\nu_i \pm \frac{1}{2}\delta\nu$) onto a cell which has been prepared to have its band gap equal to that photon energy, i.e., $\hbar\nu_i = \epsilon_g^i$, as in Fig. 1(c). Such an array of cells can, in principle, cover the solar spectrum such that there is no phonon emission loss. However, the losses due to radiative recombination are still present and represent a major, in principle, loss mechanism.

To put this in perspective, we quote from an excellent recent review [5] of the physics of photovoltaic conversion: "That leaves radiative recombination as the major [energy loss] process. Can this be avoided? The answer is no. If a radiative upward transition to generate the excitation is allowed, its reversal, the radiative downward transition must be allowed as well." In support of the "no" answer, we note that the "detailed balance" argument quoted above is the basis for the original Shockley-Quiesser analysis. They say [3]: "in order to find the upper theoretical limit for the efficiency of *p*-*n* junction solar cell convertors, a limiting efficiency called the detailed balance limit of efficiency has been calculated for an ideal case in which

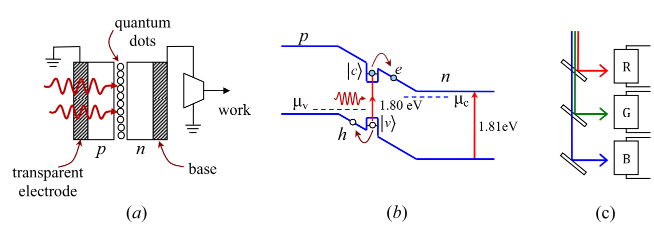


FIG. 1 (color online). (a) Schematic of photocell consisting of quantum dots sandwiched between $p$ and $n$ doped semiconductors. Monochromatic solar radiation excites electrons from the $|v\rangle$ to $|c\rangle$ states in the quantum dots. (b) Chemical potentials $\mu_v$ and $\mu_c$ are indicated by dashed lines. The "built-in" field in the depletion layer separates electrons and holes; however, they can radiatively recombine before being separated. Absorption in the bulk semiconductor is avoided by ensuring that $\hbar\nu < \epsilon_g$; e.g., in the figure we choose $\hbar\nu = 1.80$ eV and $\epsilon_g = 1.81$ eV. (c) The energy loss by phonon emission from electrons excited well above the band edge can be essentially eliminated by dividing the photon flux into frequency components, each of which is directed to a cell with its band gap matched to the incident light. For example frequency sensitive beam splitters are here depicted as dividing the solar radiation into red, green, and blue beams which are tuned to the three cells with $\hbar\nu_i \approx \epsilon_g^i$ where $i = R, G,$ and $B$.

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the only recombination mechanism of electron hole pairs is radiative as required by the principle of detailed balance."

Indeed it was on this basis of such detailed balance arguments that Einstein introduced the concept of stimulated emission in the early part of the twentieth century. And when we have population inversion, i.e., negative temperatures [6], laser or maser action obtains [7]. However, by the end of the century, it was predicted theoretically [8] and demonstrated experimentally [9] that it is possible to break detailed balance and cancel stimulated absorption, while keeping stimulated emission, yielding LWI.

For example it is shown in Ref. [8(b)] that when the ground state is a doublet coherently driven by a microwave field, as in Fig. 2(a), it is possible to cancel or reduce absorption. Physically, this lack of absorption is a manifestation of quantum interference. When an atom makes a transition from the upper level to the two lower levels, the total transition probability is the sum of the $a \rightarrow b$ and $a \rightarrow c$ probabilities [see Fig. 2(a)]. However, transition probabilities from the two lower levels to the single upper level are obtained by squaring the sum of the two probability amplitudes. This makes possible lasing even if there is no population inversion.

More interesting in the present context, is the fact that it is possible to prepare a coherent doublet in the excited state and again break detailed balance, but this time we work to cancel stimulated and spontaneous emission while keeping absorption. Thus, in the notation of Fig. 2(b), we now have the possibility of altering the balance between emission and absorption and reducing radiative recombination while keeping absorption intact.

We set the stage by first giving a pico review of single frequency photocell behavior with radiative recombination. That is, we calculate the efficiency of a cell contained in an optical cavity (such as a photonic crystal) [10] and illuminated by monochromatic light which is tuned near the band edge so that $\hbar\nu = \epsilon_c - \epsilon_v$ in the notation of Fig. 1(b).

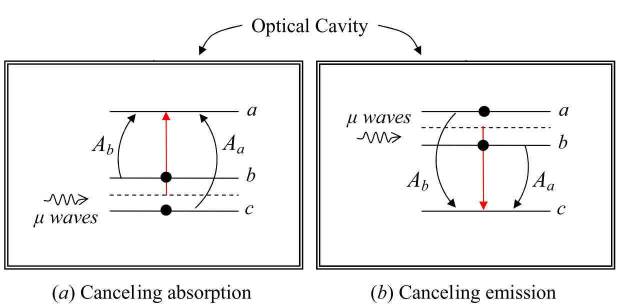


FIG. 2 (color online). (a) Atoms in coherent superposition of ground states $b$, $c$ which are driven by microwaves. The radiation indicated by the lighter (red) line draws equally from levels $b$ and $c$. The probability of exciting the level $a$ goes as the square sum of the sum of the probability amplitudes, i.e., $P_{\mathrm{absorb}} = |A_a + A_b|^2$, and can be zero. The probability of emission goes as $P_{\mathrm{emission}} = |A_a|^2 + |A_b|^2$ and does not vanish. This is the basis for lasing without inversion. (b) The use of quantum coherence in the excited state doublet $a$, $b$ makes possible the opposite behavior, i.e., cancellation of emission but not absorption.

Next, in order to explore how quantum coherence could (in principle) be used to mitigate radiative recombination in a solar cell, let us first analyze the quantum dot cell of Fig. 1, in which we inject monochromatic radiation resonant with the energy $\epsilon_c - \epsilon_v$. The populations $N_v$ and $N_c$ are described by the chemical potential $\mu_v$ and $\mu_c$ and the ambient temperature $T_a$ so that

$$\frac{N_v}{N_c} = \exp[\epsilon_c - \epsilon_v - (\mu_c - \mu_v)]/kT_a \tag{1}$$

and the cell voltage is $eV = \mu_c - \mu_v$.

The interaction between the quantum dots and the single mode cavity field is given by

$$V = \sum_j \hbar g_j |v_j\rangle\langle c_j| \hat{a}^\dagger + \text{adj.}, \tag{2}$$

where $g_j$ is the coupling constant between the $j$th quantum dot, and the radiation field is described by the creation (annihilation) operators $\hat{a}^\dagger(\hat{a})$. For the present purposes we may model the problem assuming the density matrix for the field, $\rho$, evolves dynamically as

$$\dot{\rho} \cong -\int_{t_0}^{t} \frac{dt'}{\hbar^2} \sum_{j,\alpha_j} \langle \alpha_j | [V^j(t, t_0), [V^j(t', t_0), \rho(t) \otimes \rho^j]] | \alpha_j \rangle \tag{3}$$

where $\rho^j$ is the density matrix for the $j$th dot, the states of the dot are $|\alpha_j\rangle = |c_j\rangle$ or $|v_j\rangle$ in the notation of Fig. 1(b), and $t_0$ is the time that the $j$th dot is excited by thermal phonon excitation from the $n$ type (donor) or $p$ type (acceptor) reservoir having chemical potential $\mu_c$ or $\mu_v$. Upon excitation to the states $|c_j\rangle$ and $|v_j\rangle$ the electrons are modeled as decaying back to the $n$ type or $p$ type reservoir at rate $\gamma$. We may include this process by simply taking $V^j(\tau, t_0) \rightarrow V^j(\tau, t_0)\exp[-\gamma(\tau - t_0)]$ where $\tau = t$ or $t'$ as it appears in Eq. (3). The summation over dots is replaced by $\sum_j = r\int_{-\infty}^{t} dt_0$, and Eqs. (1)–(3) yield

$$\begin{aligned}\dot{\rho}(a, a^\dagger, t) = -\kappa[&\rho_{cc}(aa^\dagger\rho + \rho aa^\dagger - 2a^\dagger\rho a) \\ &+ \rho_{vv}(a^\dagger a\rho + \rho a^\dagger a - 2a\rho a^\dagger)],\end{aligned} \tag{4}$$

where $r$ is the rate of scattering of electrons (into and out of the dots) and $\kappa = -rg^2/\gamma^2$.

The equation of motion for the average photon number $\dot{\bar{n}} = \mathrm{Tr}[a^\dagger a\dot{\rho}(a, a^\dagger, t)]$ can then be calculated from Eq. (4); we find

$$\dot{\bar{n}} = -(R_v - R_c)\bar{n} + R_c \tag{5}$$

$$= -R\left[\frac{1}{e^{\hbar\nu/kT_s} - 1} - \frac{1}{e^{(\hbar\nu - eV)/kT_a} - 1}\right], \tag{6}$$

where $R_v = \kappa\rho_{v,v}$, $R_c = \kappa\rho_{c,c}$, $R = R_c - R_v$, and $T_s(T_a)$

is the temperature of the solar radiation (ambient surroundings). Please note that we adhere to the convention that all frequencies are circular frequencies so that $\hbar\nu$ (not $h\nu$) is the photon energy.

In going from (5) to (6) we have replaced $\bar{n}$ on the right-hand side by its equilibrium value for solar radiation at temperature $T_s$. The second term in the square bracket follows from the fact that $R_v/R_c = \exp(\hbar\nu - eV)/kT_a$ since $\rho_{v,v}/\rho_{c,c} = N_v/N_c$ as it appears in Eq. (1).

As an example of the utility of Eq. (6), we note that at steady state, the second term in the square bracket cancels the first term so that $\hbar\nu/kT_s = (\hbar\nu - eV)/kT_a$, which implies [1]

$$eV = \hbar\nu\left(1 - \frac{T_a}{T_s}\right). \tag{7}$$

Having seen that our toy model contains the essential features of monochromatic photocell operation, we proceed to replace the state $|c\rangle$ by the doublet $|c_1\rangle$, $|c_2\rangle$ which is coupled by a resonant driving field with $\hbar\nu_0 = \frac{1}{2}(\epsilon_{c1} - \epsilon_{c2})$, as in Fig. 3(a).

The classical driving field couples the levels $|c_1\rangle \equiv |1\rangle$ and $|c_2\rangle \equiv |2\rangle$ of Fig. 3(a) with Rabi frequency $\Omega$. To model this we add a driving term to Eq. (3) given by $V^j = \frac{1}{2}\hbar\Omega[|1_j\rangle\langle 2_j|e^{-i\varphi} + \text{adj.}]$ and then transform the driving field away to obtain a new interaction Hamiltonian which treats $\Omega$ to all orders. We make the secular approximation such that we ignore terms like $e^{i(\Omega+\Delta_1)t}$, compared to $e^{i(\Omega-\Delta_1)t}$, where $\Delta_1 = \omega_1 - \nu$. In the case of resonance such that $\Omega = \Delta_1$ and, for simplicity, taking $\Omega > \gamma$, we may write the interaction as

$$\mathcal{V} = \frac{\hbar g}{2}[(1 - e^{-i\varphi})|v\rangle\langle 2| + (1 + e^{+i\varphi})|v\rangle\langle 1|]a^\dagger + \text{adj.}, \tag{8}$$

where the phase $\varphi$ is governed by the driving field.

We then obtain a photon rate equation for the quantum dot photocell depicted in Fig. 3(a), and find that the (monochromatic) radiation injected in the cavity is now described by the equation of motion

$$\dot{\bar{n}} = -[\mathcal{R}_v - (\mathcal{R}_c^{(1)} + \mathcal{R}_c^{(2)})]\bar{n} + (\mathcal{R}_c^{(1)} + \mathcal{R}_c^{(2)}), \tag{9}$$

where, for the present toy model [11], we may write

$$\mathcal{R}_v = 2\kappa\rho_{v,v}, \tag{10}$$

$$\mathcal{R}_c^{(1)} = \kappa\rho_{1,1}(1 + \cos\varphi), \tag{11}$$

$$\mathcal{R}_c^{(2)} = \kappa\rho_{2,2}(1 - \cos\varphi), \tag{12}$$

in which the matrix elements coupling $|c_1\rangle$ and $|c_2\rangle$ to $|v\rangle$ are taken as equal (and real), $\varphi$ is the phase of the driving field, and for typographical convenience we set $\rho_{c_1,c_1} = \rho_{1,1}$ and $\rho_{c_2,c_2} = \rho_{2,2}$. From Eqs. (11) and (12) we see that, for example, when $\varphi = 0$ and $\rho_{1,1} \to 0$, then the recombi-

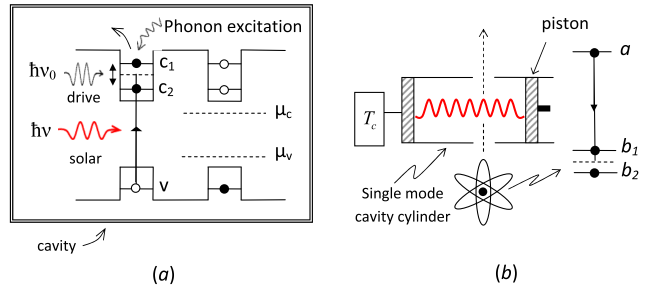


FIG. 3 (color online). (a) Quantum dots having upper level conduction band states, $|c_1\rangle$ and $|c_2\rangle$, are coherently driven by a field such that $\hbar\nu_0 = \frac{1}{2}(\epsilon_{c_1} - \epsilon_{c_2})$. The monochromatic solar photons having energy $\hbar\nu$ are tuned to the midpoint between the upper levels. The host semiconductor system, in which the quantum dots are embedded, has effective Fermi energies $\mu_c$ and $\mu_v$ for the conduction and valence bands. (b) A single mode photo-Carnot engine in which the working photon "fluid" is heated by quantum fuel consisting of atoms having quantum coherence induced between the lower levels.

nation rates $\mathcal{R}_c^{(1)}$ and $\mathcal{R}_c^{(2)}$ vanish. In any case, the second term in Eq. (6) is replaced so that

$$\frac{1}{e^{(\hbar\nu - eV)/kT_a} - 1} \to \frac{1}{e^x - 1}, \tag{13}$$

where

$$e^x = 2\rho_{v,v}/[\rho_{1,1} + \rho_{2,2} + (\rho_{11} - \rho_{22})\cos\varphi]. \tag{14}$$

In the incoherent case, $\langle\cos\varphi\rangle = 0$ and

$$e^x = \frac{2\rho_{v,v}}{\rho_{1,1} + \rho_{2,2}} \cong \frac{\rho_{v,v}}{\rho_{c,c}} = e^{(\hbar\nu - eV)/kT_a} \tag{15}$$

which implies the usual result Eq. (7). In the coherent case, when $\varphi = \pi$, Eq. (14) yields

$$e^x = \frac{\rho_{v,v}}{\rho_{1,1}} = e^{(\hbar\tilde{\nu} - eV)/kT_a}, \tag{16}$$

where $\tilde{\nu} = \nu + \nu_0$.

Thus Eq. (6) now reads

$$\dot{\bar{n}} = -\mathcal{R}\left[\frac{1}{e^{\hbar\nu/kT_s} - 1} - \frac{1}{e^{(\hbar\nu + \hbar\nu_0 - eV)/kT_a} - 1}\right], \tag{17}$$

which implies

$$eV = \hbar\nu\left(1 - \frac{T_a}{T_s}\right) + \hbar\nu_0. \tag{18}$$

That is, we now have a quantum efficiency which exceeds the voltage given by Eq. (7) [12].

The preceding coherent drive model illustrates the role of quantum coherence in a simple way. However, it is possible to generate coherence $\rho_{1,2}$ without the use of an external field. For example, quantum noise induced coherence via Fano coupling [13] yields a result essentially equivalent to (18).

Furthermore, the power generated by a Fano effect quantum dot photocell arrangement [similar to Fig. 3(a) without the drive field] can be substantially enhanced [14] as compared to the "two level" toy solar cell of Fig. 1(b).

Finally we make contact with the quantum Carnot engine [15], which is in some ways similar to the quantum solar cell. In Fig. 3(b), the photo-Carnot cycle heat engine of [15] is shown with a single mode field as the working fluid. If the field is maintained at thermal equilibrium by hot atoms injected into the cavity, then the engine operates with the usual Carnot efficiency $\eta = 1 - \frac{T_c}{T_h}$, where $T_h$ and $T_c$ are the temperatures of the hot energy source and the cold entropy sink. However, if the atoms are injected in a coherent superposition of levels $b_1$ and $b_2$ as in Fig. 3(b), then, as shown in [5,15], the efficiency of this quantum photon engine is given by

$$\eta_Q = \eta - 3\frac{T_c}{T_h}\bar{n}|\rho_{1,2}|\cos\varphi, \tag{19}$$

where $\varphi$ is defined by $\rho_{1,2} = |b_1||b_2|e^{i\varphi}$. The correspondence with the quantum photocell is clear: In the present Letter, we use quantum coherence to enhance the transfer of solar energy to the quantum dots. In the quantum photo-Carnot engine, we use quantum coherence to maximize transfer of atomic energy to the photons.

To summarize, we return to the question, "Can radiation recombination be avoided?" The answer is yes, in principle. By breaking detailed balance, radiative rec ombinations can be substantially reduced. This can, in principle, enhance the efficiency of photocells, e.g., photodetectors and solar cells; however this is not our key point. It is important to understand the fundamental limits and that radiative recombination can be mitigated.

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[11] We have not included the Stefan-Boltzmann factors and have assumed focused radiation. Reference [1(a)] deals with these issues. Likewise, the form of Eqs. (11) and (12) is chosen for simplicity. Other models and other approximations yield other forms for (11) and (12).

[12] It should be noted that the energy absorbed from the drive field connecting $|2\rangle \leftrightarrow |1\rangle$ is of the order $\hbar\nu_0$ or greater. The states $|c_1\rangle$ and $|c_2\rangle$ are to a good approximation in thermal equilibrium. The drive field will induce coherence between these states much as in the case of nuclear magnetic resonance, as will be discussed further elsewhere. Likewise, the coupling of solar energy into a photonic crystal will be discussed further in a later paper.

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[14] In a future paper, we shall derive an enhanced power generation following the treatment given in M. O. Scully *Coherent Control, Fano Interference, and Non-Hermitian Interactions*, Workshop held in May, 1999 (Kluwer Academic Publishers, Norwell, MA, 2001).

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