Using Quantum Coherence to Improve the Efficiency of Quantum Heat Engines

Marlan Scully

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Quantum Heat Engine Power Increased by Quantum Coherence

Marlan Scully




with K. Chapin, K. Dorfman, B. Kim, and A. Svidzinsky
Texas A&M University and Princeton University

Quantum Coherence Can Improve Quantum Heat Engine (QHE) Efficiency

I. Quantum Thermodynamics

II. Photo-Carnot QHE

III. The Laser as a QHE

1. $$\frac{\hbar\nu_{laser}}{\hbar\nu_{pump}} = 1 - \frac{T_c}{T_h}$$ From Detailed Balance

2. Quantum Coherence Can Improve Laser QHE Quantum Efficiency by Breaking Detailed Balance

IV. The Photocell as a QHE

1. $$\frac{eV}{\hbar\nu_{pump}} = 1 - \frac{T_c}{T_h}$$ From Detailed Balance

2. Quantum Coherence Can Improve Photocell QHE Quantum Efficiency by Breaking Detailed Balance

V. Noise Induced Quantum Coherence Can Enhance:

1). Laser QHE Power

2). Photocell QHE Power

3). Efficiency of Photosynthesis

Heat Engines

- Classical Heat Engines produce useful work by extracting energy from a high temperature energy source and rejecting entropy to a low temperature entropy sink.
- A Photo-Carnot Engine is a Carnot cycle engine in which photons are the working fluid and the piston is driven by radiation pressure. Quantum coherence allows us to achieve thermodynamic efficiency beyond the Carnot limit without violating the second law.
- Laser and Photocell Quantum Heat Engines are driven by thermal radiation and governed by the laws of quantum thermodynamics.

Laser/Photocell Quantum Heat Engines Timeline

- 1900 Planck Entropy of Thermal Light
- 1905 Einstein Photon Concept, 1917 Stimulated Emission, Detailed Balance
- 1954 Gordon, Zeiger, and Townes First Maser
- 1959 Maser as a Quantum Heat Engine
- 1994 TAMU Lasing Without Inversion
- 2003 Photo-Carnot Quantum Heat Engine
- 2010 Photocell Quantum Efficiency Improved by Quantum Coherence
- 2011 Laser and Photocell Quantum Heat Engines

Quantum Thermo I

Planck studies Entropy of Light to Arrive at the Quantum*

Wein Entropy

$$\frac{\partial^2 S}{\partial \bar{\varepsilon}^2} = -\frac{1}{b\omega\bar{\varepsilon}}$$

where $\bar{\varepsilon}$ = average energy of oscillator with frequency ω

Planck Entropy 1900

$$\frac{\partial^2 S}{\partial \bar{\varepsilon}^2} = -\frac{k_B}{\bar{\varepsilon}(\hbar\omega - \bar{\varepsilon})} \Rightarrow \bar{\varepsilon} = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

*Planck Photon Statistics and Bose Einstein condensation, Progress in Optics 2007

Quantum Thermo II

Einstein studies Entropy of Light to Arrive at the Photon*

Fluctuations

$$\frac{\left\langle (\Delta E)^2 \right\rangle}{(\hbar\omega)^2} = \underbrace{\bar{n}^2}_{\text{wave}} + \underbrace{\bar{n}}_{\text{particle}}$$

Wave Particle Duality 1905

***Progress in Optics 2007**

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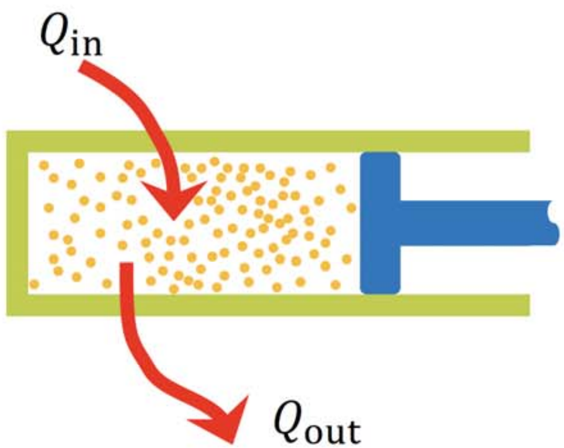
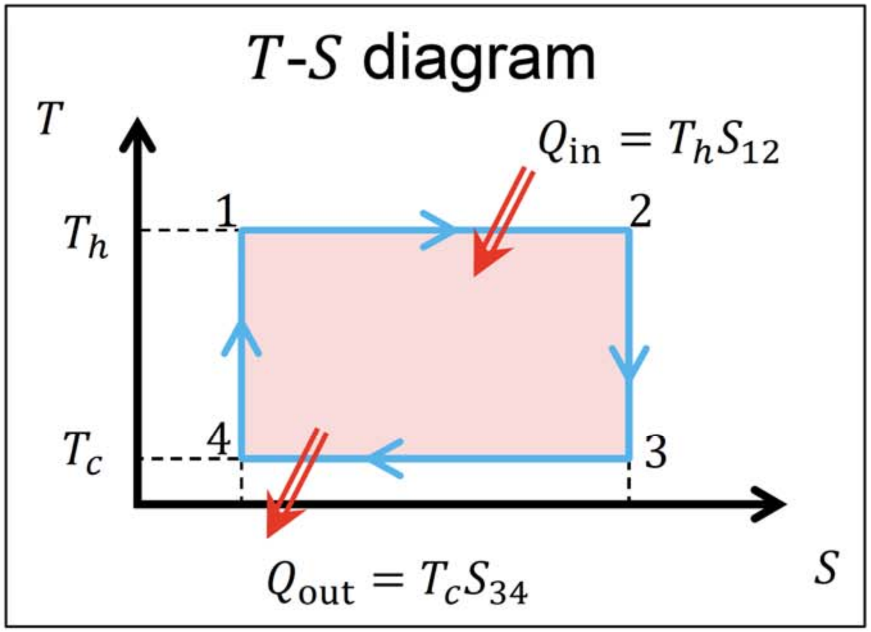
Carnot Efficiency





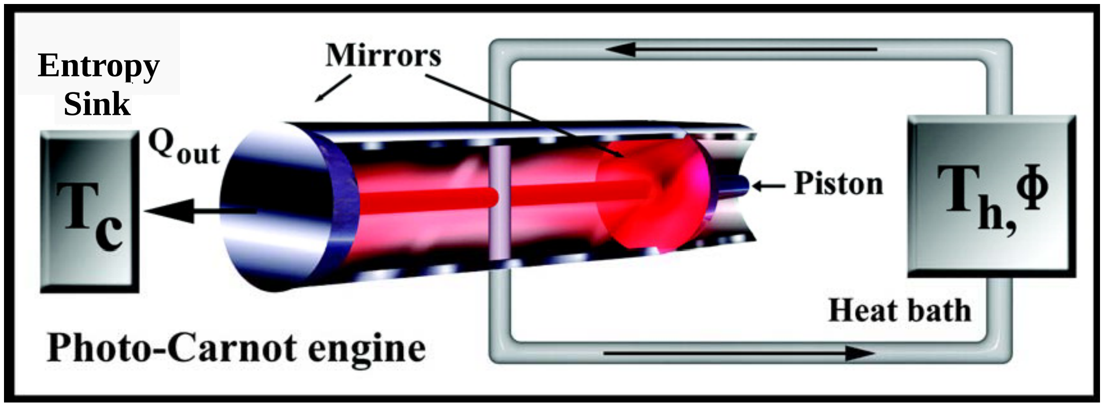
thermal efficiency

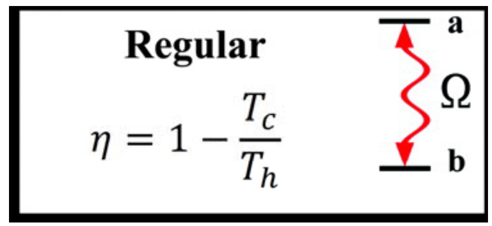
$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_h S_{12} - T_c S_{34}}{T_h S_{12}} = 1 - \frac{T_c}{T_h}$$

Photo-Carnot Engine

- Working Fluid(radiation) heated by two-level atoms

$$PV = \hbar\Omega\bar{n}$$





Science AAAS

Extracting Work from a Single Heat Bath via Vanishing Quantum Coherence

M. Scully, M. Zubairy, G. Agarwal, and H. Walther

Science **299**, 862 (2003);
DOI: 10.1126/science.1078955

Single Mode = Single Atom

$$PV = kT \qquad \text{(One atom)}$$

$$PV = \hbar\Omega\bar{n} \qquad \bar{n} = \frac{kT}{\hbar\Omega}$$

$$= kT \qquad \text{(One mode)}$$

$$\eta_c = 1 - \frac{T_c}{T_h}$$

Rate equation for photon number (I)

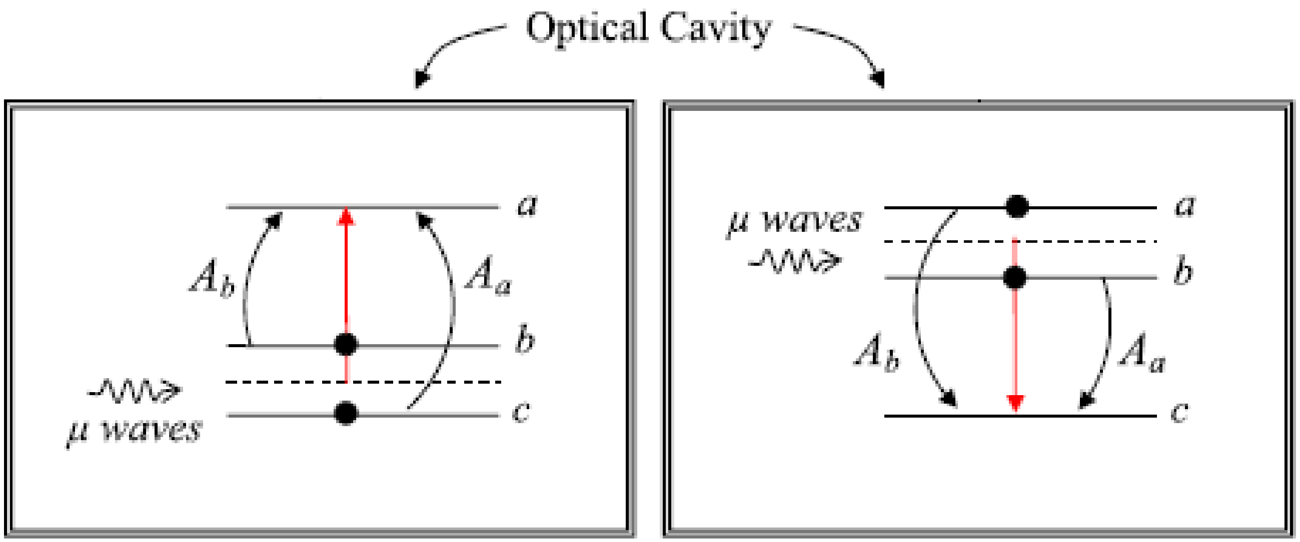
- With two-level atoms field,

$$\dot{\bar{n}} = \alpha[\rho_{aa}(\bar{n}+1) - \rho_{bb}\bar{n}]$$

- The steady-state solution is

$$\bar{n} = \frac{1}{\frac{\rho_{bb}}{\rho_{aa}} - 1} = \frac{1}{\exp(\hbar\Omega/kT_h) - 1} \xrightarrow[\hbar\Omega/kT_h \ll 1]{\text{high tempearture}} \frac{kT_h}{\hbar\Omega}$$

Lasing Without Inversion



(*a*) Canceling absorption (*b*) Canceling emission

(a) Use of quantum coherence in ground state *b*,*c* to cancel absorption

(b) the use quantum coherence in the excited state *a*,*b* to cancel emission

$$\dot{\bar{n}}_{laser} = \alpha(\bar{n}+1)(|A_a|^2 + |B_b|^2) - \alpha\bar{n}|A_a + B_b|^2$$

VOLUME 76, NUMBER 12 PHYSICAL REVIEW LETTERS 18 MARCH 1996

Laser Oscillation without Population Inversion in a Sodium Atomic Beam

G. G. Padmabandu,[1,2,*] George R. Welch,[1,2] Ivan N. Shubin,[1] Edward S. Fry,[1,2,†] Dmitri E. Nikonov,[1,2,‡]
Mikhail D. Lukin,[1,2] and Marlan O. Scully[1,2,3]
[1]*Texas Laser Laboratory, Houston Advanced Research Center, The Woodlands, Texas 77381*
[2]*Department of Physics, Texas A&M University, College Station, Texas 77843-4242*
[3]*Max-Planck-Institut für Quantenoptik, D-85748 Garching, Germany*
(Received 29 August 1995)

Continuous wave (cw) amplification and laser oscillation without population inversion have been observed for the first time in a Λ scheme within the sodium D_1 line. This is also the first demonstration in which the lasing medium was an atomic beam; this is
the physics, lays a foundation for extensions into the ult
structure were critical to the choice of experimental appr
matrix calculations and clearly show there was no populat

"Continuous wave (cw) amplification and laser oscillation without population inversion have been observed…"

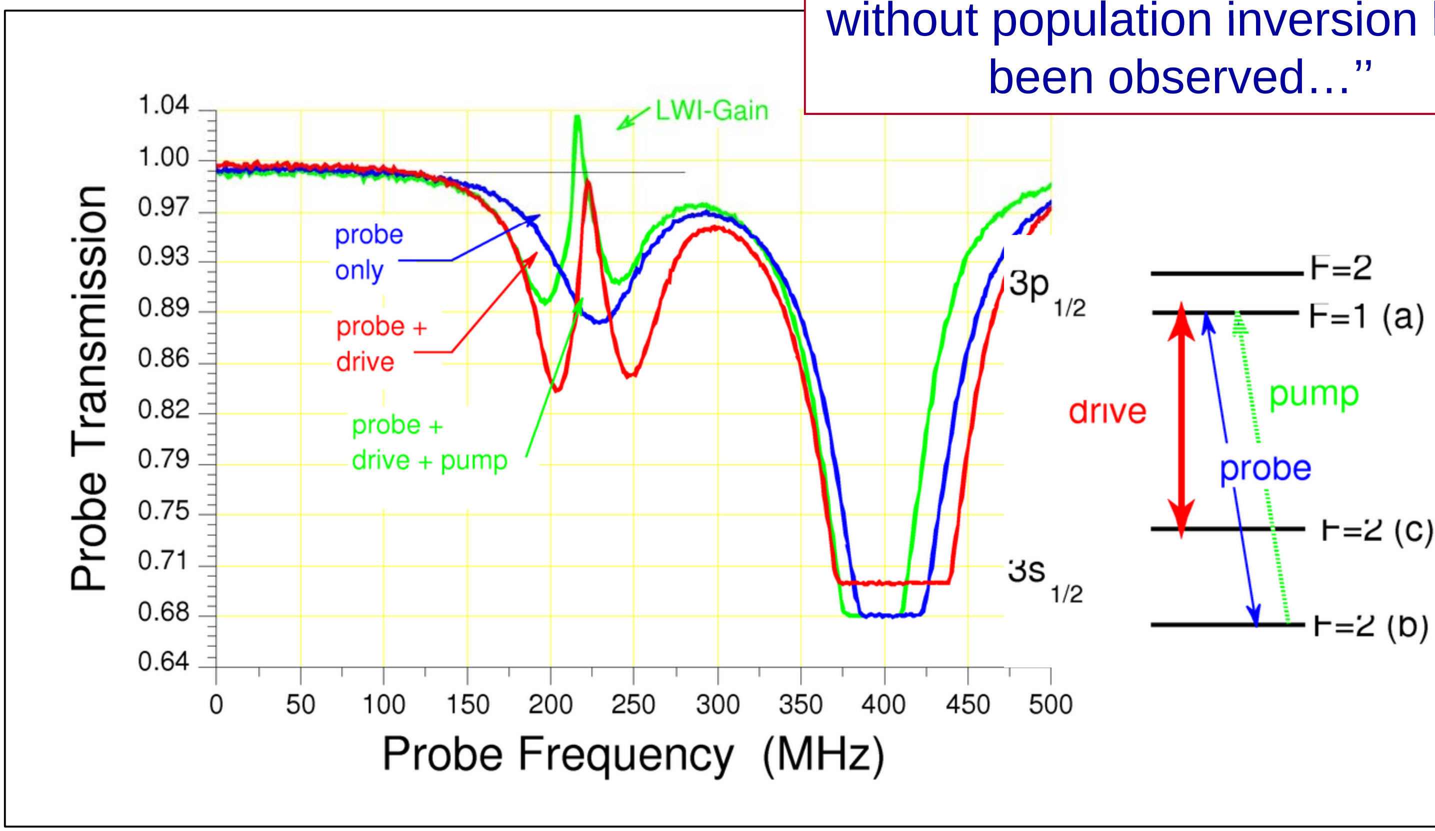
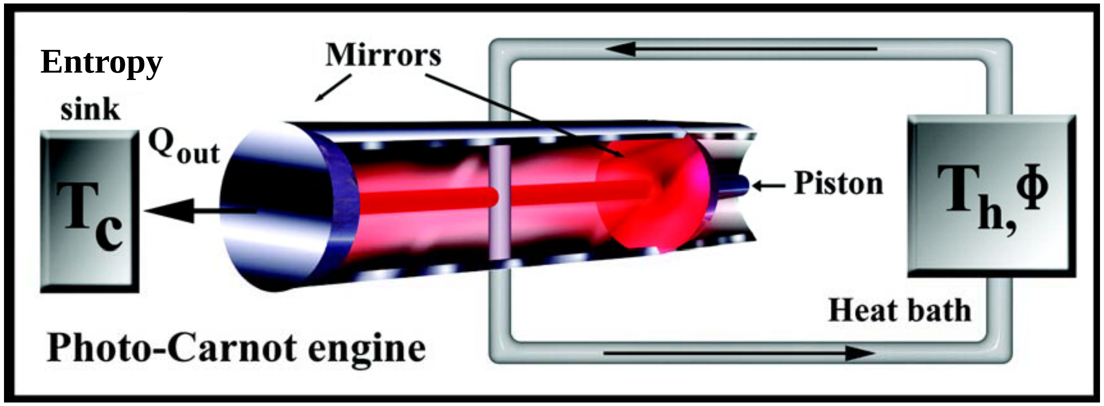
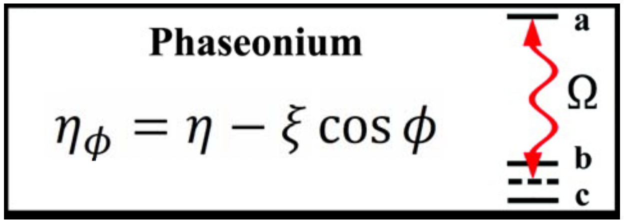


Photo-Carnot Engine

- Working Fluid heated by phaseonium





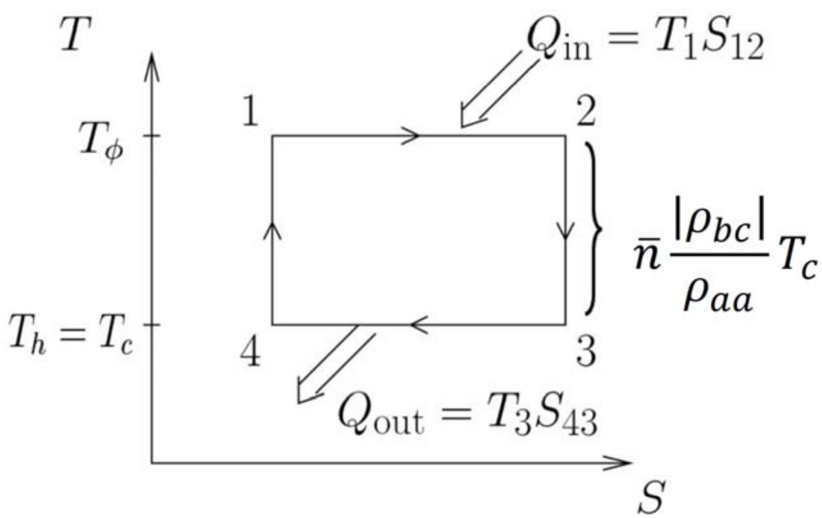
Rate equation for photon number (II)

- With phased three level atoms(phaseonium) field,
  $\dot{\bar{n}}_\phi = \alpha\left[2\rho_{aa}(\bar{n}_\phi + 1) - (\rho_{bb} + \rho_{cc} + \rho_{bc} + \rho_{cb})\bar{n}_\phi\right]$
- The steady-state solution is

$$\bar{n}_\phi \xrightarrow[\hbar\Omega/kT_h \ll 1]{\text{high tempearture}} \frac{kT_h}{\hbar\Omega}\left(1 - \bar{n}\frac{|\rho_{bc}|}{\rho_{aa}}\cos\phi\right) \equiv \frac{kT_\phi}{\hbar\Omega}$$

T_ϕ : effective radiation temperature

Efficiency of a Quantum Carnot Engine



Temperature-entropy diagram for Carnot cycle engine.

In the present QHE, Q_{in} is provided by the hot atoms.

When $T_h = T_c$, the photo-Carnot engine can still produce useful work if the coherent three-level heat bath atoms are "phased" such that $\phi = \pi$.

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}}$$

$$\eta_\phi = \frac{T_\phi S_{12} + T_c S_{43}}{T_\phi S_{12}} = \eta - \frac{T_c}{T_h}\bar{n}\frac{|\rho_{bc}|}{\rho_{aa}}\cos\phi$$

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Quantum Heat Engine
with and without Quantum Coherence

- Laser Q. H. E.

✓ Laser Q.H.E. by Scovil and Schulz-DuBois

✓ Lasing without inversion

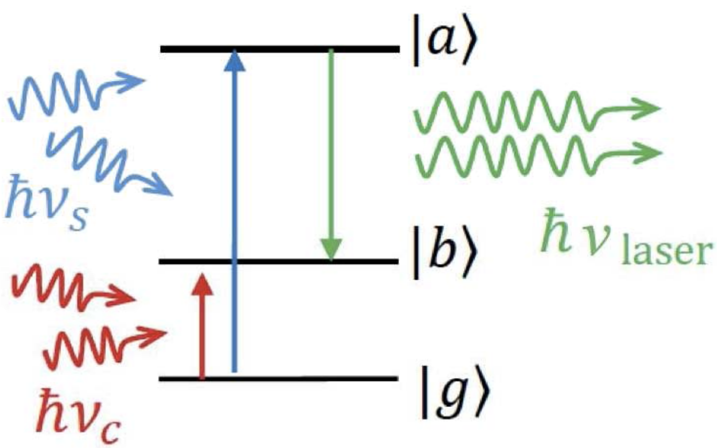
✓ Supercharged Quantum heat engine

Laser Quantum Heat Engine (QHE)

PRL **2**, 262 (1959) PHYSICAL REVIEW LETTERS MARCH 15, 1959

THREE-LEVEL MASERS AS HEAT ENGINES*

H. E. D. Scovil and E. O. Schulz-DuBois
Bell Telephone Laboratories,
Murray Hill, New Jersey
(Received January 16, 1959)



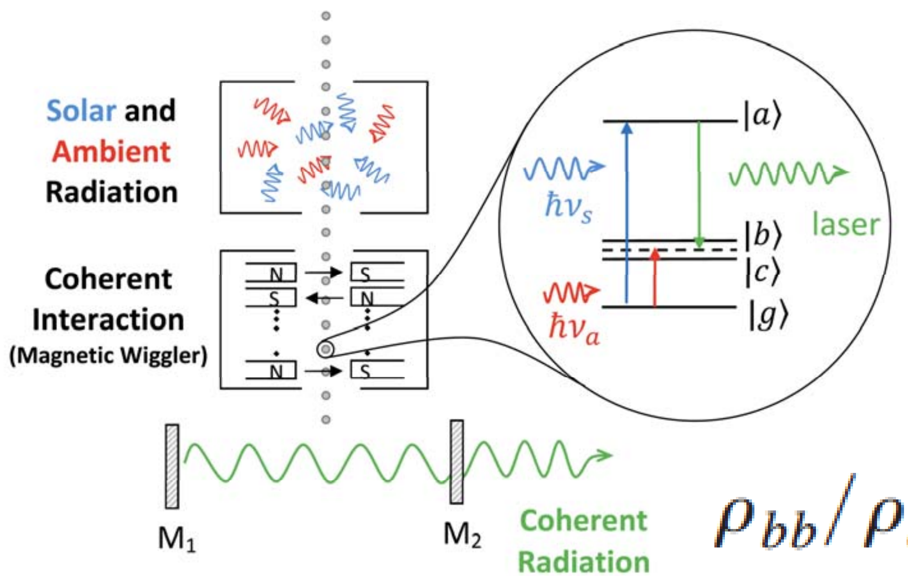
Boltzmann distribution

$$\frac{n_b}{n_a} = \frac{n_b}{n_g} \cdot \frac{n_g}{n_a} = e^{-\hbar\nu_c/kT_c} \cdot e^{\hbar\nu_s/kT_h}$$

At threshold (n_b=n_a) efficiency of maser QHE

$$\frac{\hbar\nu_\ell}{\hbar\nu_s} = 1 - \frac{T_c}{T_s}$$

PRL **106,** 049801 (2011) PHYSICAL REVIEW LETTERS week ending 28 JANUARY 2011



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$$\rho_{bb}/\rho_{aa} = \exp-[\epsilon_b/kT_c - \epsilon_a/kT_h]$$

$$\dot{\mathcal{E}} = \kappa(2\rho_{aa} - \rho_{bb} - \rho_{cc} - \rho_{bc} - \rho_{cb})\mathcal{E}$$

At threshold

$$\frac{\hbar\nu_\ell}{\hbar\nu_s} = \eta_{\mathrm{Carnot}} + \delta\eta \qquad \delta\eta = kT_c|\rho_{bc}|/\hbar\nu_s\rho_{aa}$$

Summary

- Efficiency from QHE can exceed the classical Carnot Efficiency by using phased three-level atoms.
- The Photo-Carnot QHE can produce work from a single thermal bath.
- Efficiency of Laser QHEs can be increased by quantum coherence.

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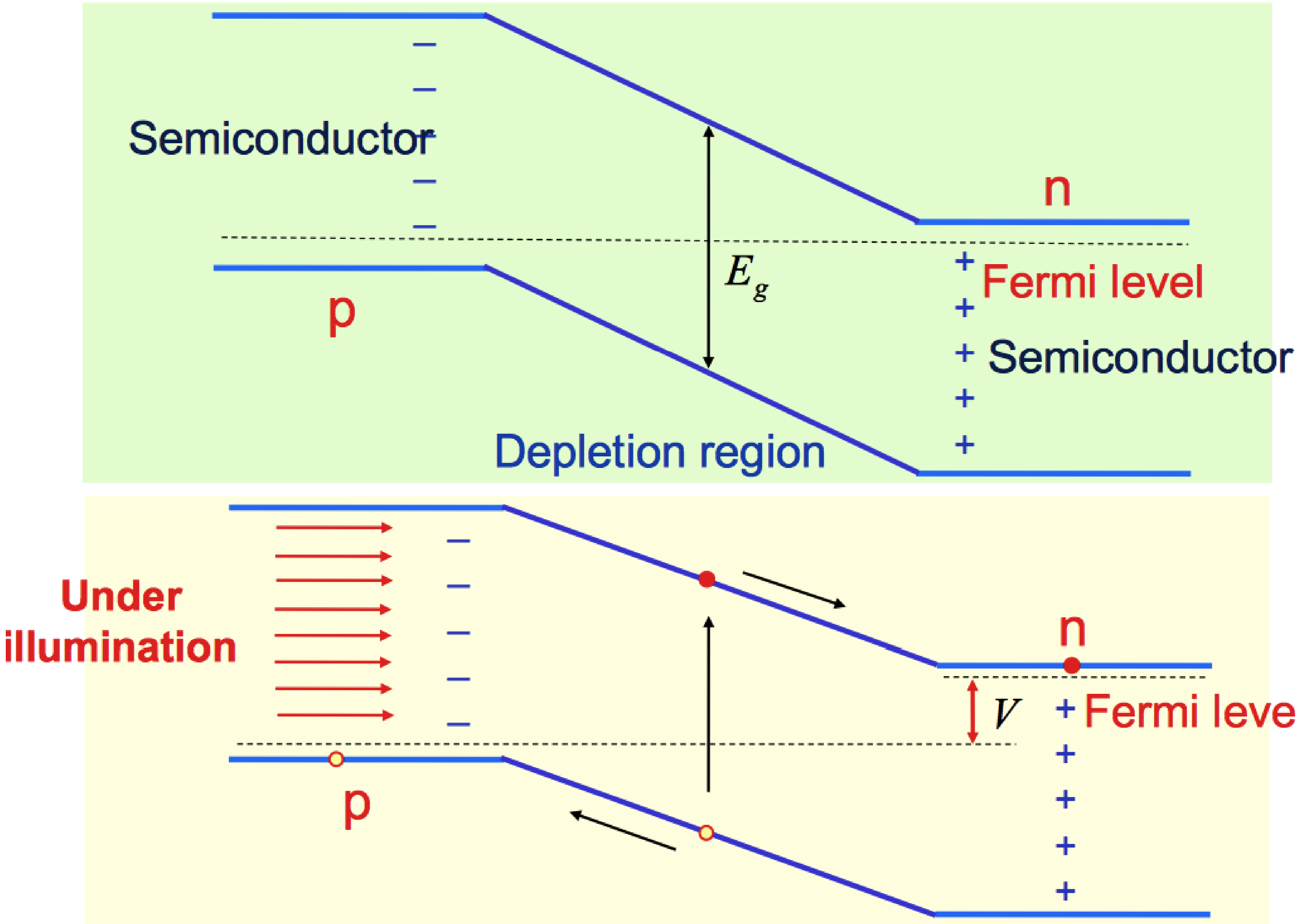
Photovoltaics Enhanced by Microwave Induced Quantum Coherence

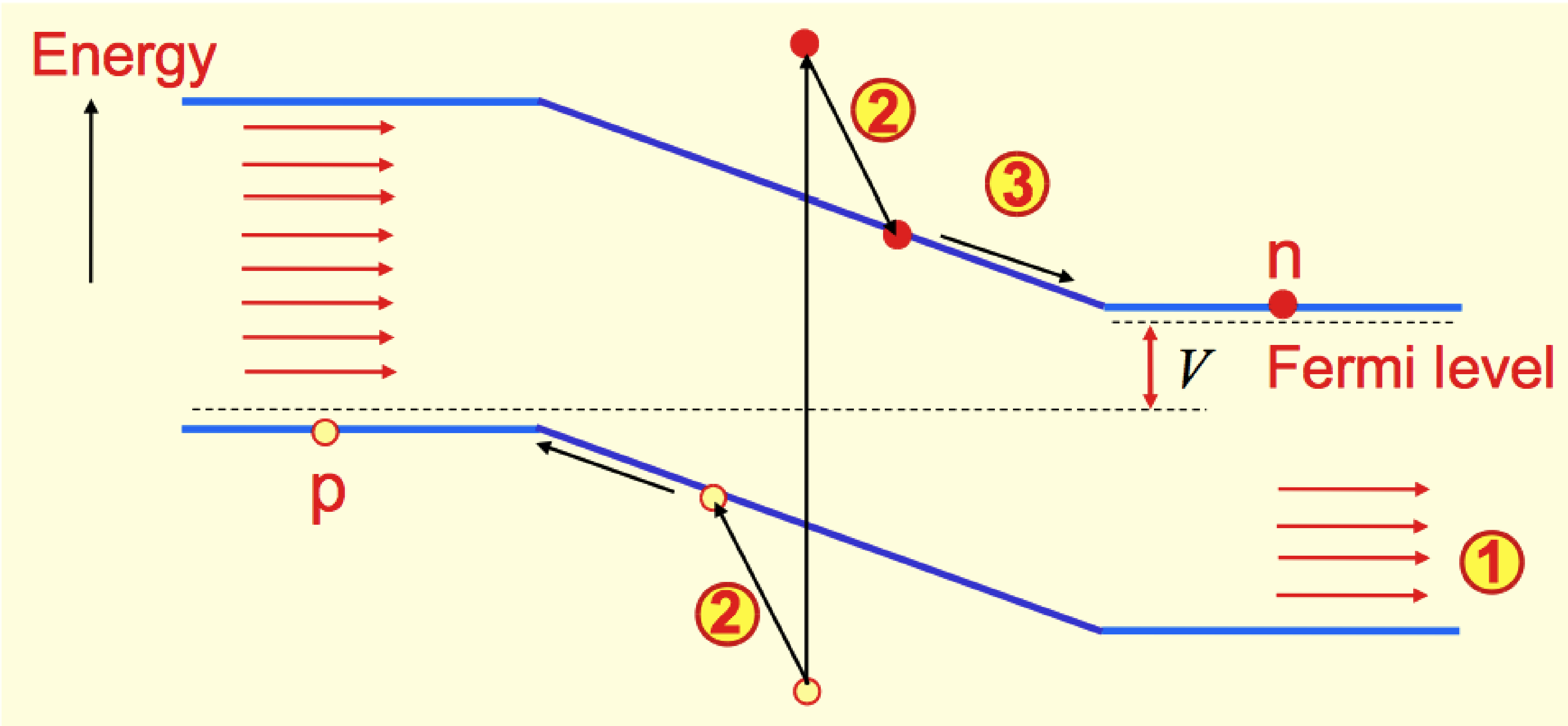
Outline

- Solar Cell Energy
- p-n Junction Photocell
  - Fundamentals
  - Shockley and Queisser's efficiency limit (detailed balance)
- Quantum efficiency enhanced by coherent driving
- Power enhanced by coherent driving
- Summary

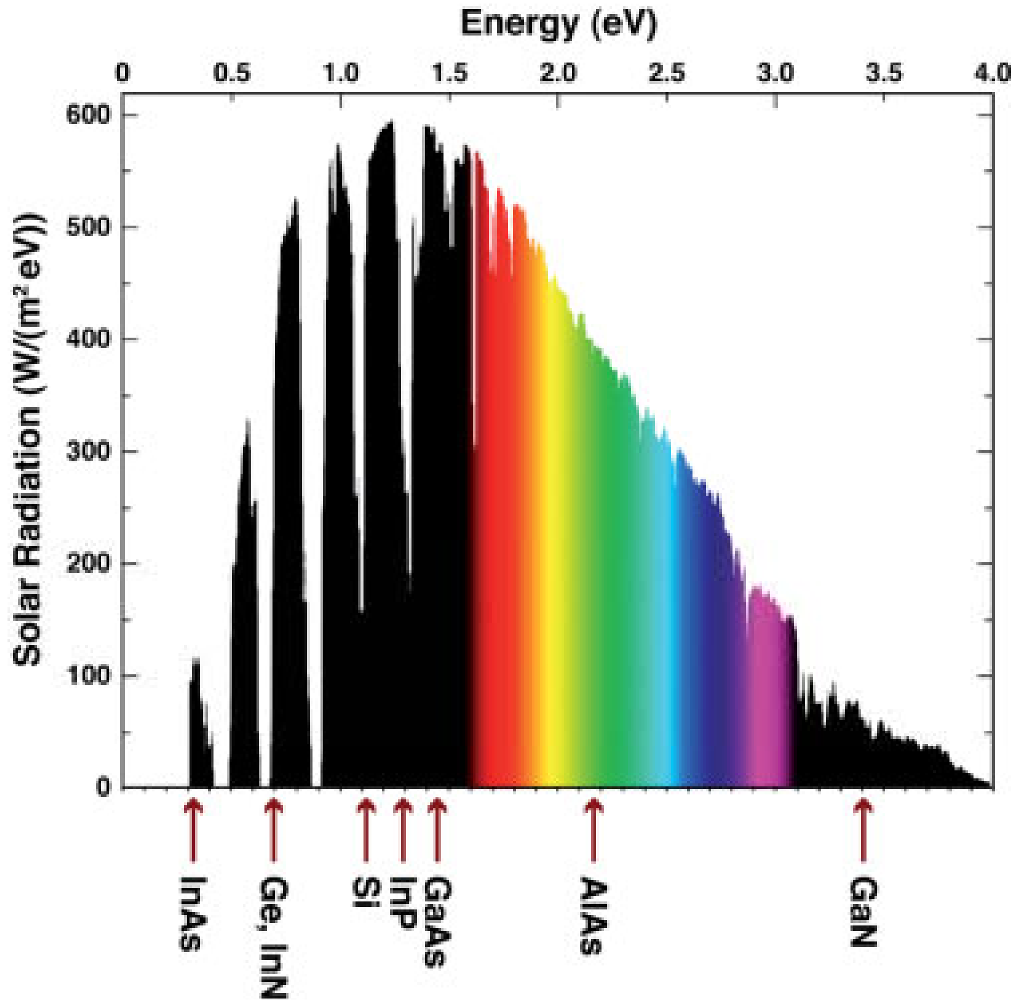
pn-junction solar cell



Solar cell losses



1. Photons with energy less then E_g are not absorbed
2. Thermal relaxation, energy is lost to phonons
3. Losses due to finite temperature of the cell (thermodynamic)

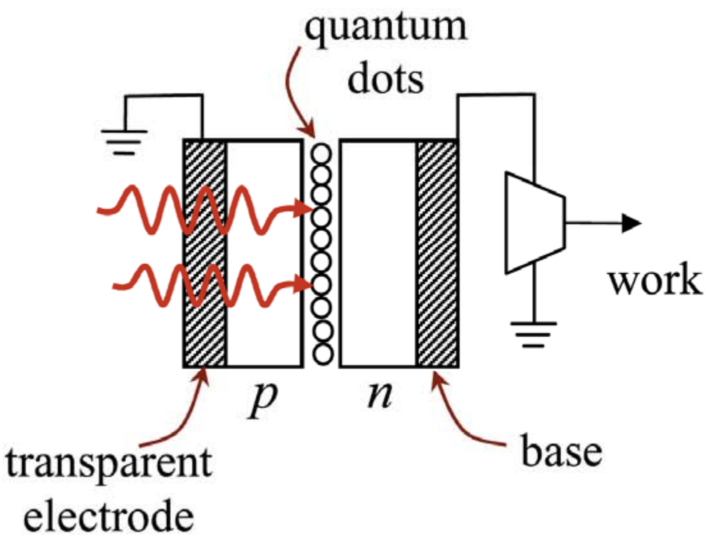


Solar spectrum with the bandgaps of semiconductors

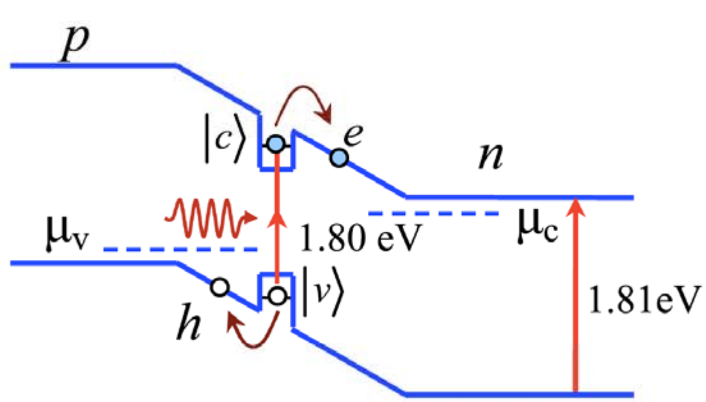
Gregory F. Brown, and Junqiao Wu, Laser & Photon Review **3**, No. 4, 394, (2009)

Quantum Dot Photo/Solar Cell

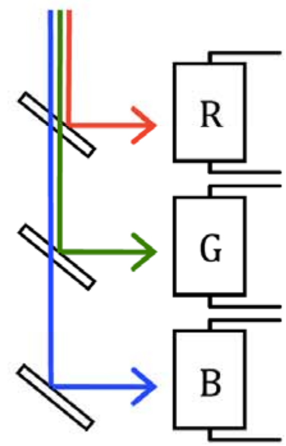
Solar cell with array of quantum dots



Electron-hole separation



Dividing photon flux onto monochromatic components



Texas A&M University

PRINCETON UNIVERSITY

Solar Cells and Detailed Balance

PRL **104,** 207701 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

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

Marlan O. Scully
Texas A&M University, College Station, Texas 77843, USA
Princeton University, Princeton, New Jersey 08544, USA
(Received 18 November 2009; published 21 May 2010)

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.

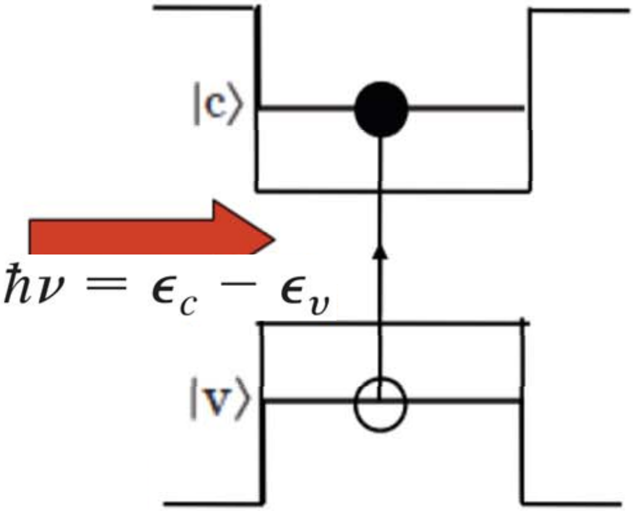
P. Würfel, *Chimia* **61**, 770 (2007)
"That leaves radiative recombination as the major [energy loss] process. Can this be avoided? The answer is no. If a radiative upward transition to generate the excitation is allowed, its reversal, the radiative downward transition must be allowed as well."

Solar cell with detailed balance

Population on levels c and v at temperature T_a

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

$$eV = \mu_c - \mu_v$$ Cell voltage



$$\hbar\nu = \epsilon_c - \epsilon_v$$

Average photon number

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

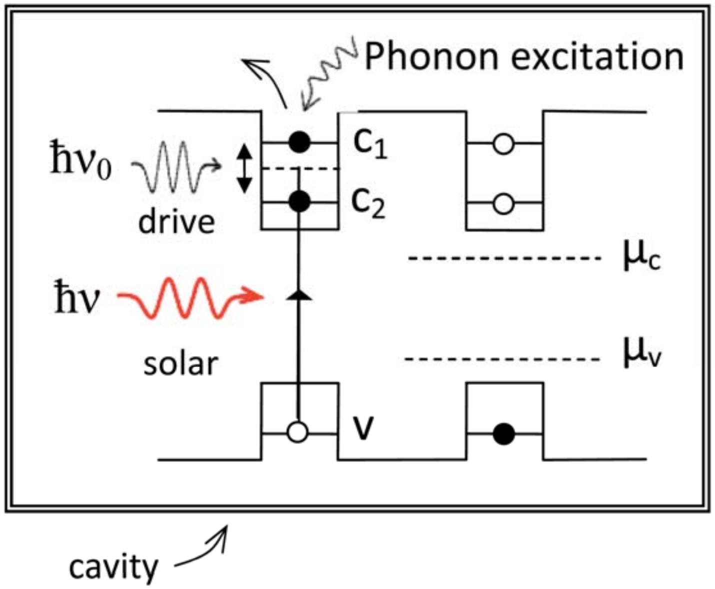
Thermodynamic efficiency

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

Solar cell with external coherence

External drive $\hbar\nu_0 = \frac{1}{2}(\epsilon_{c1} - \epsilon_{c2})$

Resonant interaction $\Omega = \omega_1 - \nu$



Average photon number

2-level 3-level

$$\frac{1}{e^{(\hbar\nu - eV)/kT_a} - 1} \rightarrow \frac{1}{e^x - 1} \qquad e^x = 2\rho_{v,v}/[\rho_{1,1} + \rho_{2,2} + (\rho_{11} - \rho_{22})\cos\varphi]$$

Thermodynamic efficiency $\varphi = \pi$

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

Detailed balance revisited

"That leaves radiative recombination as the major [energy loss] process. Can this be avoided? The answer is ~~no.~~ Yes! If a radiative upward transition to generate the excitation is allowed, its reversal, the radiative downward transition ~~must be allowed as well.~~"

can be mitigated by breaking detailed balance via quantum coherence!

Summary

- Quantum coherence induced by an external microwave field can increase the quantum efficiency (open circuit voltage) of the photocell.

- Furthermore such a coherent driven photocell generates more power. The extra power produced by the device is much larger then that derived from the microwave source which creates the coherence.

- Induced coherence results in more efficient utilization of the pump photons by increasing absorption and/or quenching unwanted emission.

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Noise induced quantum coherence

- External source:
  - ✓ Lasing Without Inversion
  - ✓ Supercharged Quantum Heat Engine
- No external field
  - ✓ Fano interference (quantum noise)
  - ✓ Agarwal (Fano-Harris) lasing without inversion

"…The preceding coherent drive model illustrates the role of quantum coherence in a simple way. However, it is possible to generate coherence without the use of an external field. For example, quantum noise induced coherence via Fano coupling…"

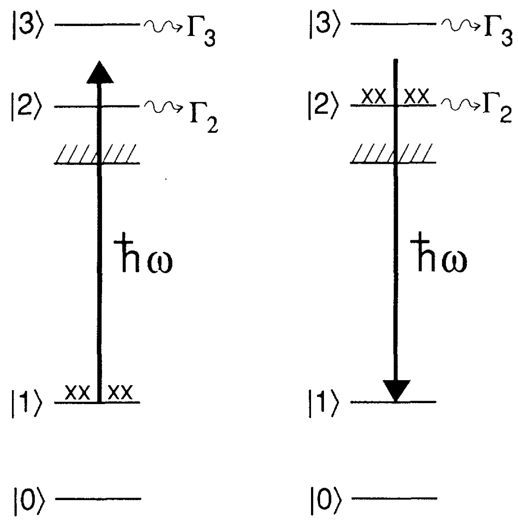
Fano Interference I. LWI

VOLUME 62, NUMBER 9 PHYSICAL REVIEW LETTERS 27 FEBRUARY 1989

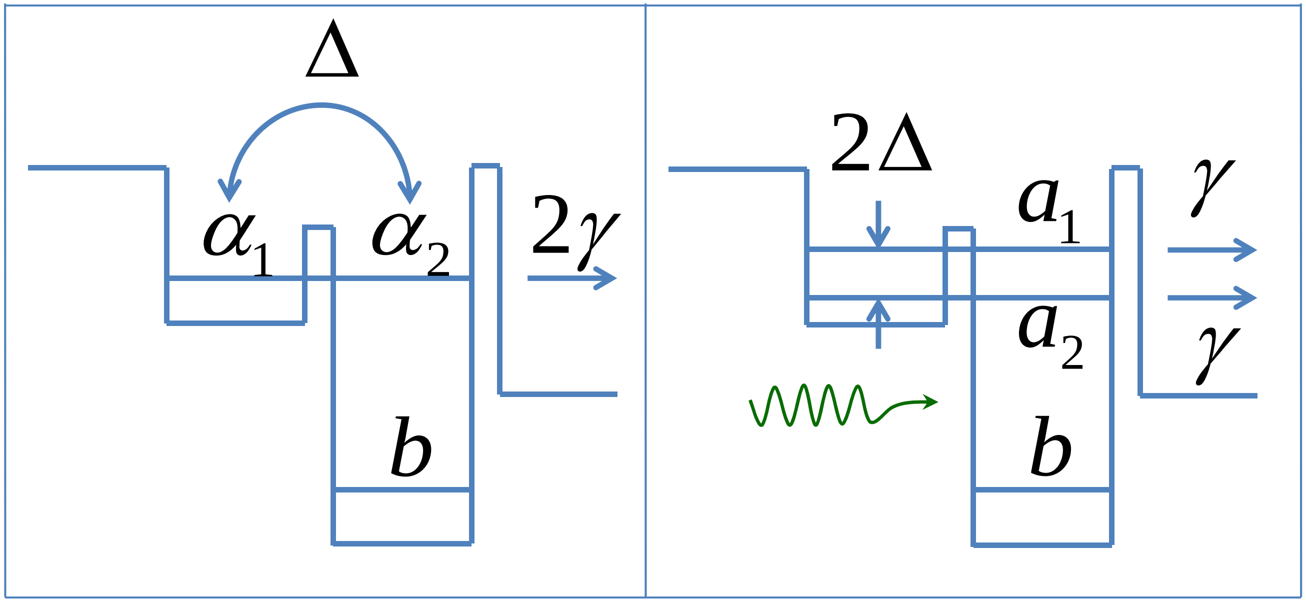
Lasers without Inversion: Interference of Lifetime-Broadened Resonances

S. E. Harris
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305
(Received 23 September 1988)

We show that if two upper levels of a four-level laser system are purely lifetime broadened, and decay to an identical continuum, then there will be an interference in the absorption profile of lower-level atoms, and that this interference is absent from the stimulated emission profile of the upper-level atoms. Laser amplification may then be obtained without inversion. Examples include interfering autoionizing levels, and tunneling systems.



Fano Interference II. Tunneling



Bare state

$$\dot{\alpha}_1 = -i\Delta\alpha_2$$

$$\dot{\alpha}_2 = -i\Delta\alpha_1 - 2\gamma\alpha_2$$

Mixing of damping terms due to Fano

$$\dot{a}_2 = -(\gamma + i\Delta)a_2 - \gamma a_1$$

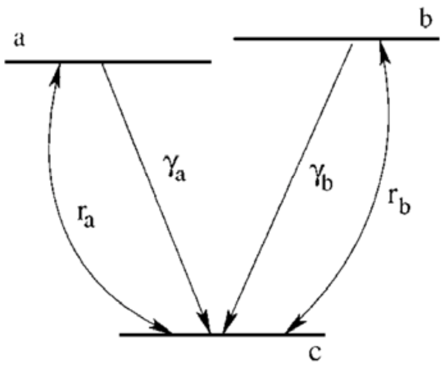
$$\dot{a}_1 = -(\gamma - i\Delta)a_1 - \gamma a_2$$

Noise induced coherence

PHYSICAL REVIEW A 74, 063829 (2006)

Inducing quantum coherence via decays and incoherent pumping with application to population trapping, lasing without inversion, and quenching of spontaneous emission

Victor V. Kozlov,[1,2] Yuri Rostovtsev,[1] and Marlan O. Scully[1,3,4]



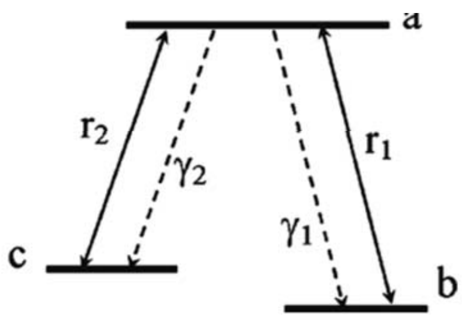
Steady state coherence

$$\rho_{ab} = \frac{p}{2}\frac{\sqrt{r_a r_b} - \sqrt{\gamma_a \gamma_b}}{r_a + r_b + \gamma_a + \gamma_b} \qquad p \equiv \frac{\mu_{ac}\mu_{bc}}{|\mu_{ac}||\mu_{bc}|}$$

Optics Communications 281 (2008) 4940–4945

Coherence induced by incoherent pumping field and decay process in three-level Λ type atomic system

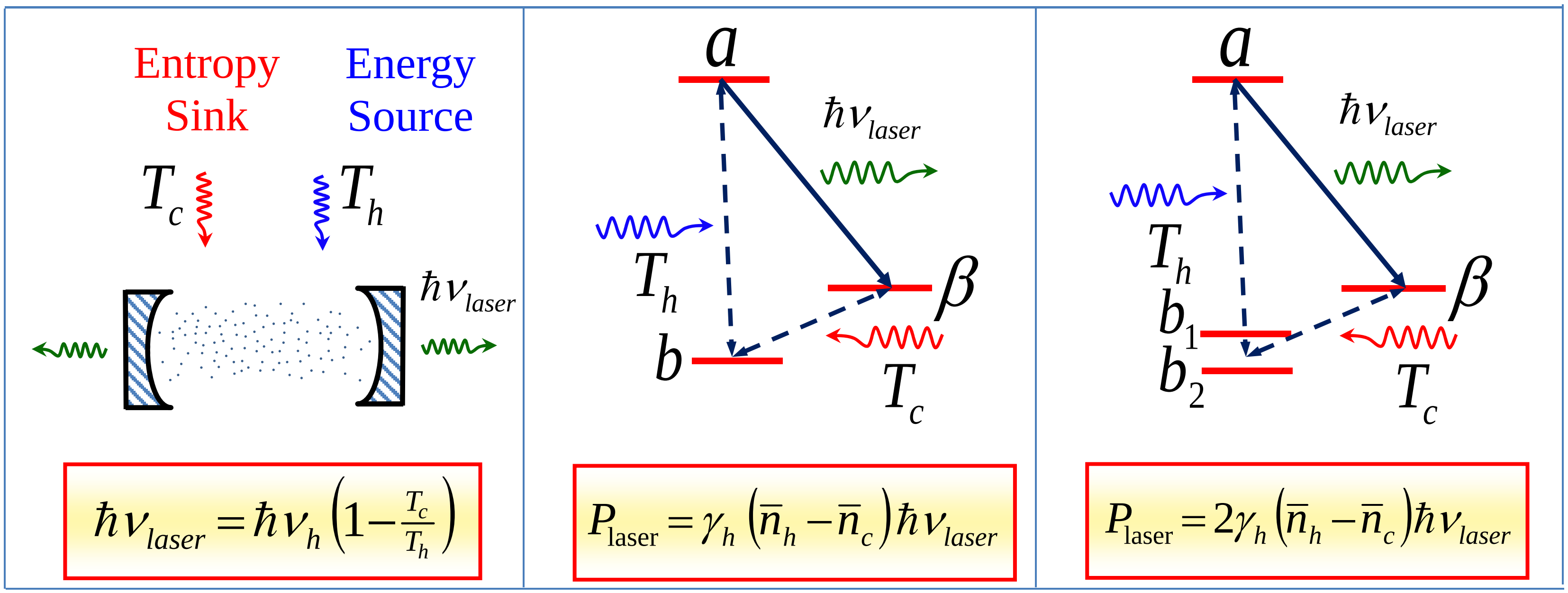
Bao-Quan Ou *, Lin-Mei Liang, Cheng-Zu Li



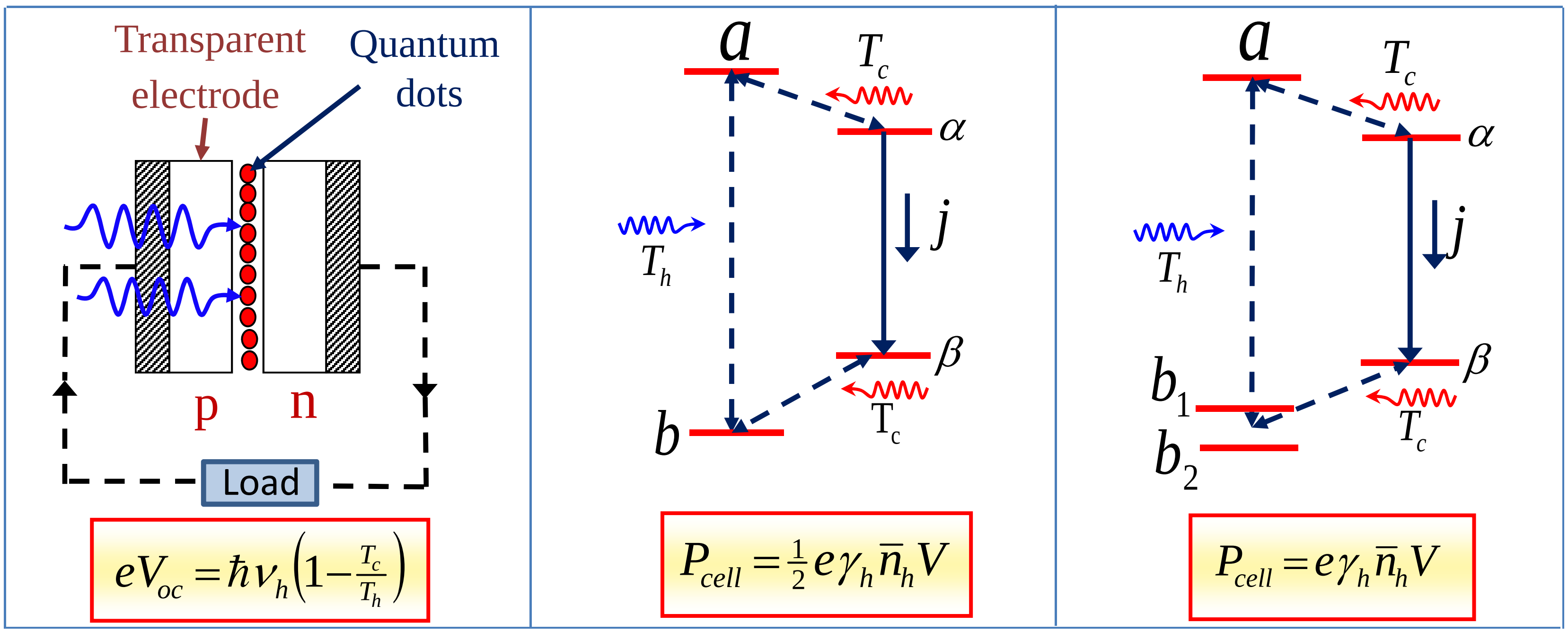
Steady state coherence

$$\rho_{bc} = -\frac{\sqrt{r_1 r_2}}{r_1 + r_2}$$

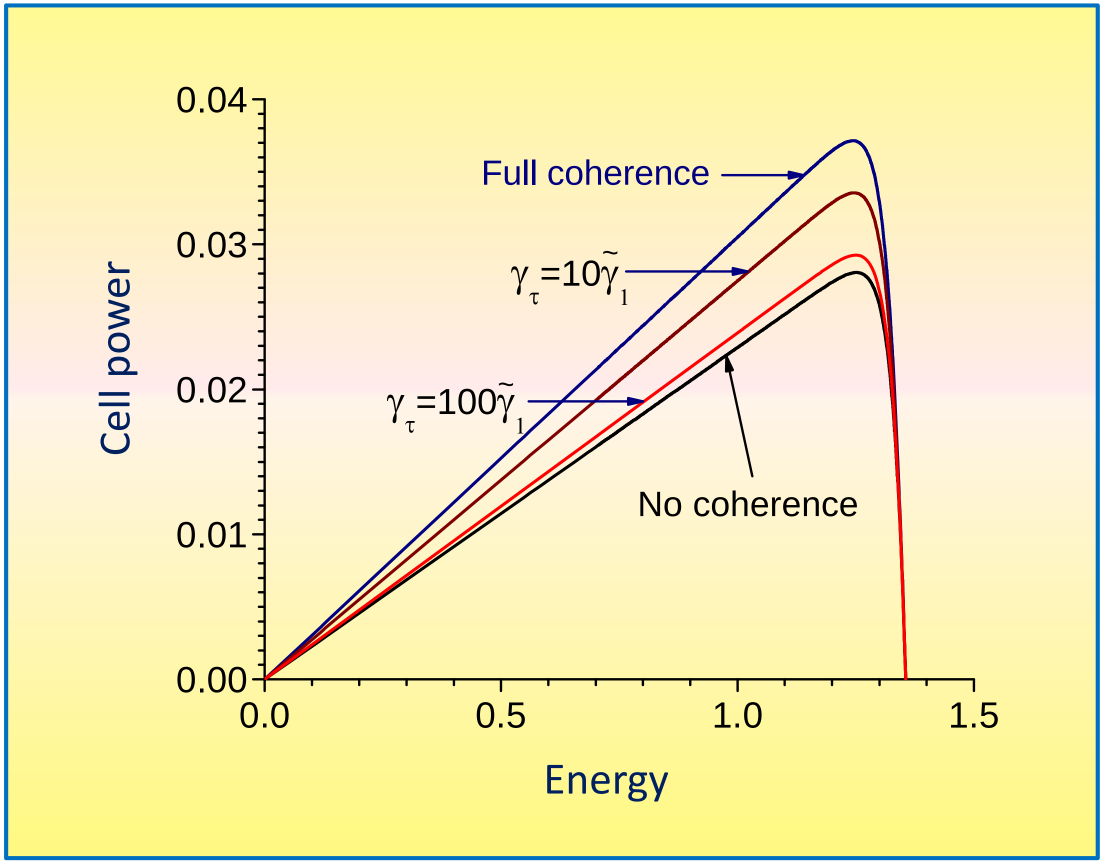
Noise induced quantum coherence can **double** the laser power at no extra cost!



Noise induced coherence can double photocell power at no extra cost!

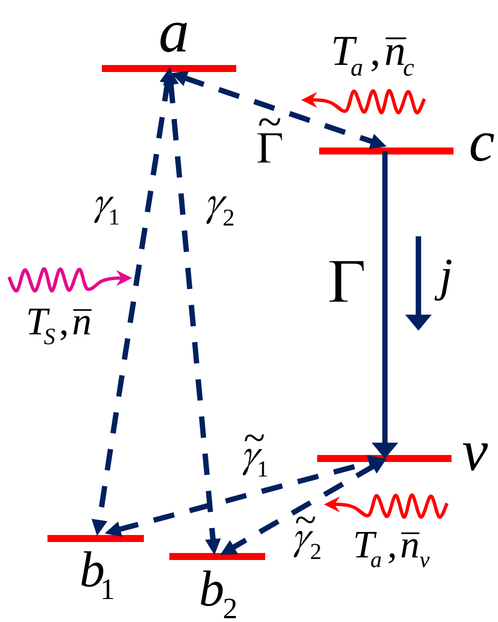


For proper cell design noise-induced coherence is **robust** against environmental decoherence



Here $\tilde{\gamma}_1$ is the fastest spontaneous decay rate. Fano interference enhances the cell power even if γ_τ is much larger than $\tilde{\gamma}_1$.

Robustness of noise induced coherence



For microwave drive with Rabi frequency Ω

$$\rho_{12} \approx \frac{i\Omega}{\gamma_\tau}$$

Noise induced coherence:

$$\rho_{12} = \frac{n_v}{4} \frac{\sqrt{\tilde{\gamma}_1 \tilde{\gamma}_2}}{\gamma_\tau + n_v \tilde{\gamma}_1 / 2}$$

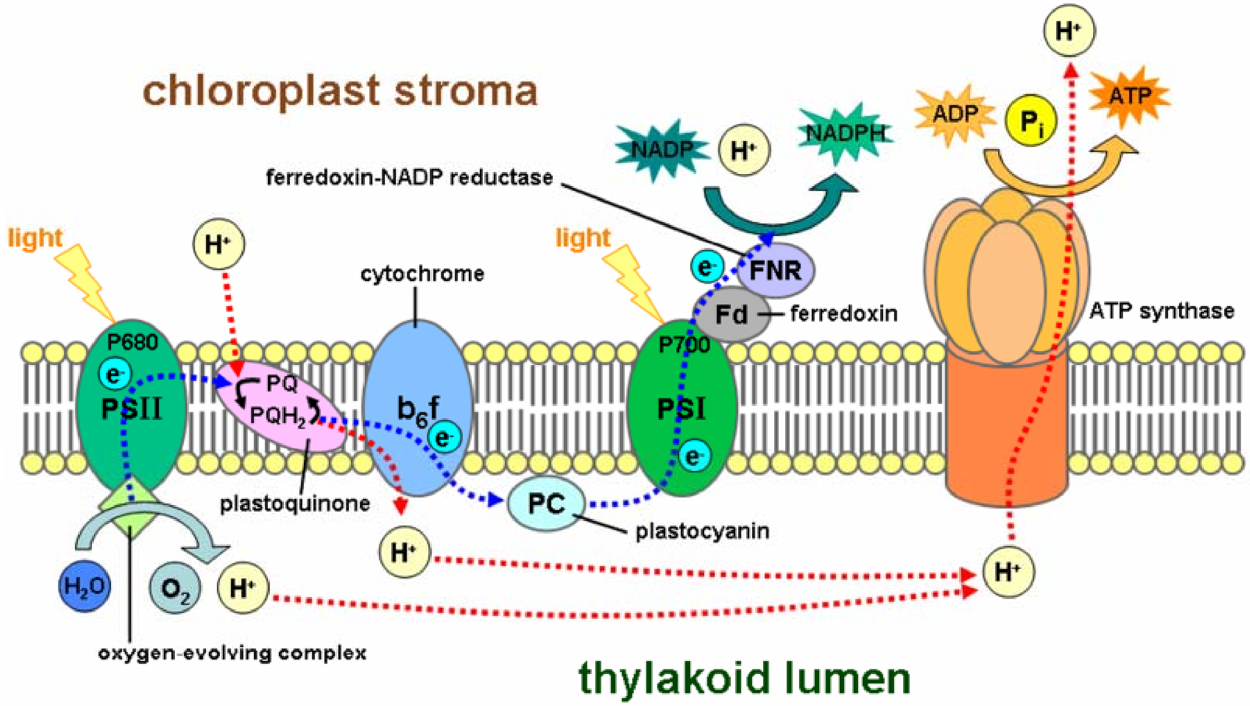
n_v is the phonon occupation number

Coherence can be large even if $\gamma_\tau \gg \tilde{\gamma}_1$ provided $n_v \gg 1$

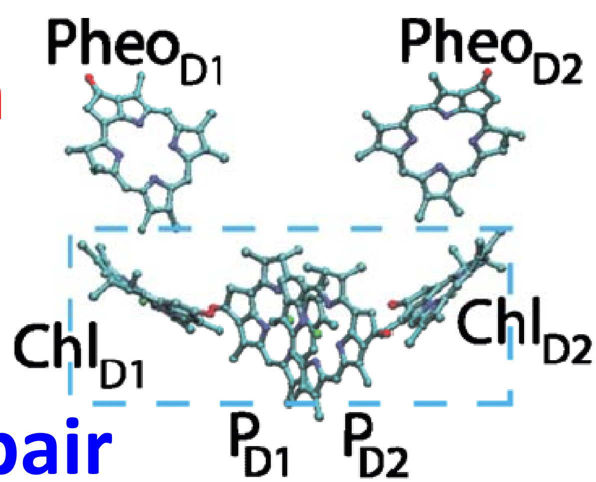
Noise induced coherence in photosynthetic systems

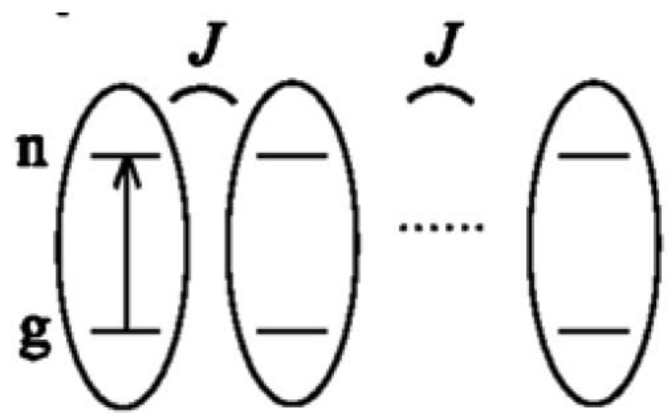
Konstantin Dorfman, Dmitri Voronine, Shaul Mukamel, and Marlan Scully

Charge separation in photosynthesis



Reaction Center of PSII





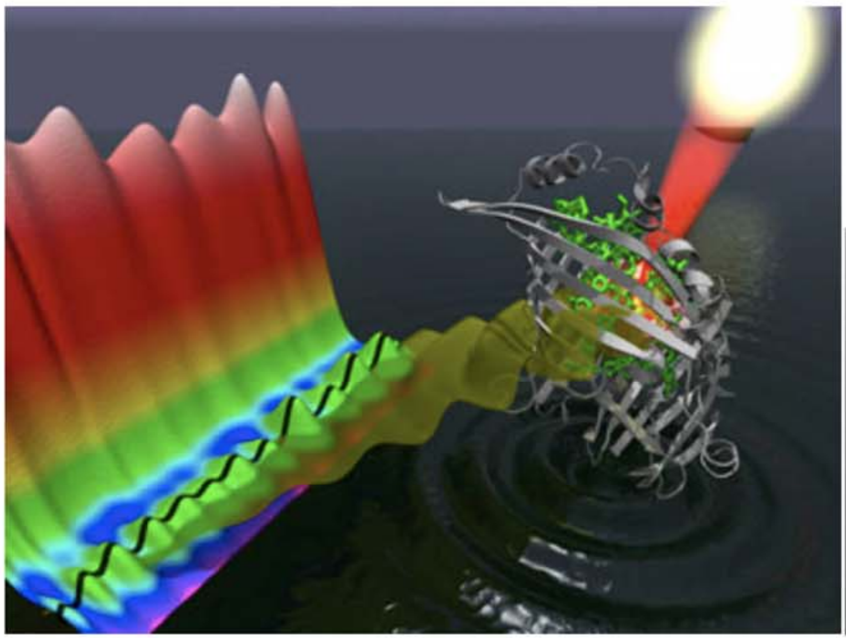
Special pair

nature Vol 446|12 April 2007|doi:10.1038/nature05678

LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Gregory S. Engel[1,2], Tessa R. Calhoun[1,2], Elizabeth L. Read[1,2], Tae-Kyu Ahn[1,2], Tomáš Mančal[1,2]†, Yuan-Chung Cheng[1,2], Robert E. Blankenship[3,4] & Graham R. Fleming[1,2]



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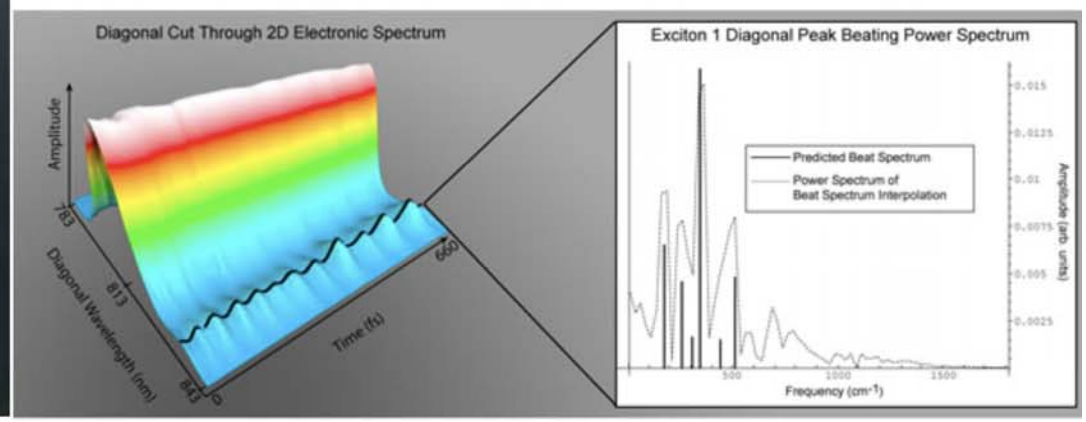
Quantum Secrets of Photosynthesis Revealed

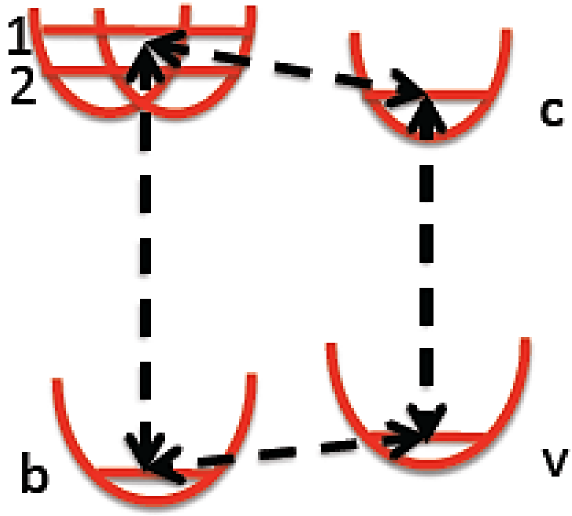


Photon echo experiments reveal quantum coherence in photosynthetic complexes

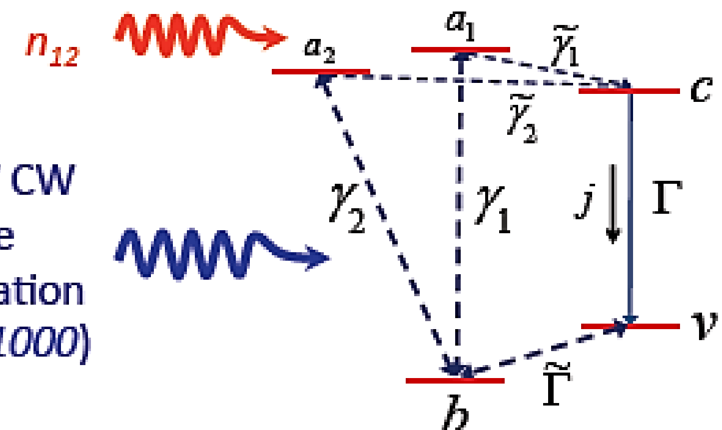
But: previous studies used lasers to induce quantum coherence.

Can we get noise-induced quantum coherence in photosynthetic complexes?

Coherence enhanced Electron flow in the Reaction Center (PS II) - Quantum Bio Heat Engine



Strong 10 mW CW thermal source Photon occupation (n_1=6000, n_2=1000)

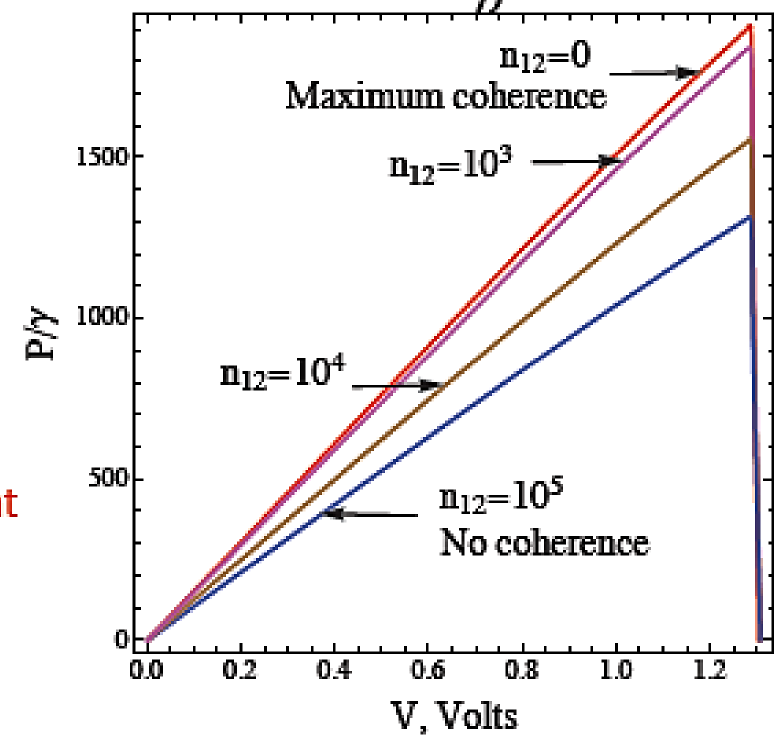


Inclusion of additional thermal source Between a_1 and a_2 ($\Gamma_{12}=10ms^{-1}$) can reduce coherence depending on number of photons n_{12}.

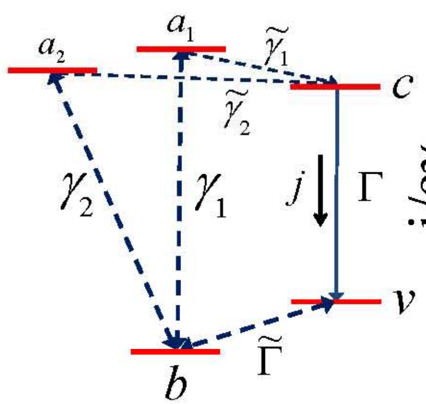
T=10K
E_a-E_b=1.7 eV
E_a-E_c=0.2 eV
E_1-E_2=10 meV (2.6ps^{-1})
E_v-E_1=0.2 eV

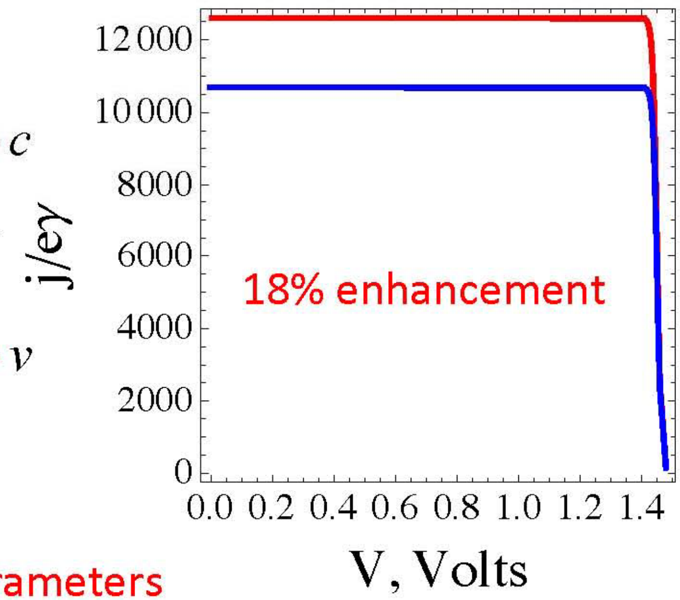
$$1/T_2 = 1.3\,\text{ps}^{-1}$$
$$\gamma_2 = 0.3\gamma_1 = 0.3\,\text{ns}^{-1}$$
$$\tilde{\gamma}_1 = 4\,\text{ps}^{-1}$$
$$\tilde{\Gamma} = 5\,\text{ps}^{-1}$$
$$\tilde{\gamma}_2 = 0.4\,\text{ps}^{-1}$$

46% enhancement compare to no interference

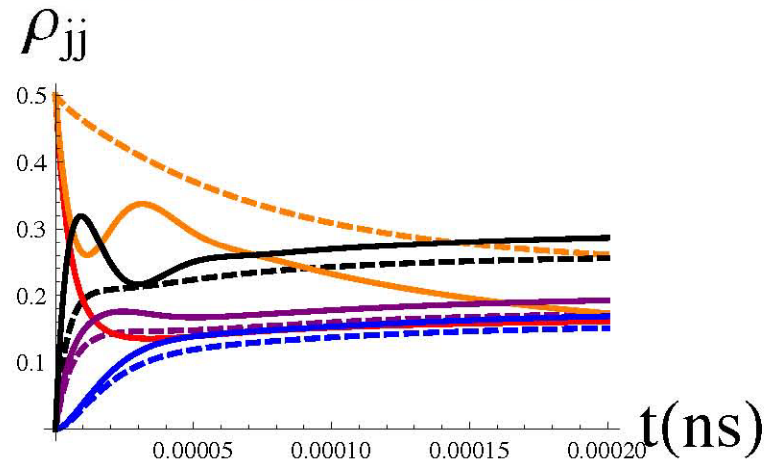


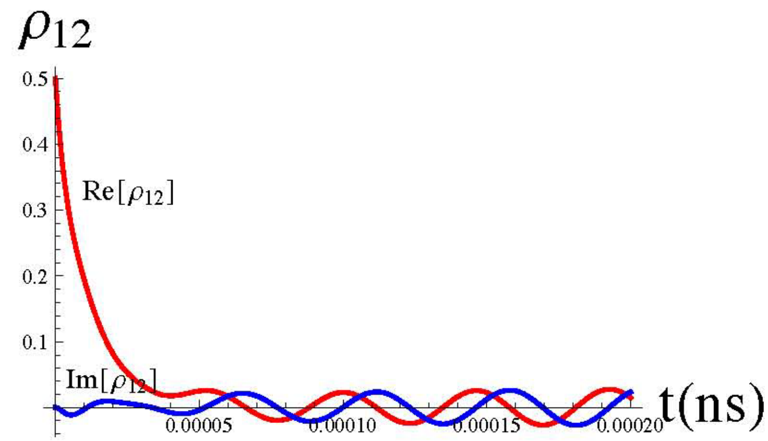
Oscillation of populations and current enhancement





Dashed – no coherence
Solid – maximum coherence





Parameters

T=77K

$T_2 = 130\text{fs}$

$\gamma_1 = \gamma_2 = 0.005\text{cm}^{-1}$

E_1= 15000cm^{-1}

E_1-E_2=600cm^{-1}

$\tilde{\gamma}_1 = 280\text{cm}^{-1}$

N_1=9n_2=90000

$\tilde{\gamma}_2 = 3.5\text{cm}^{-1}$

$\tilde{\Gamma} = 300\,\text{cm}^{-1}$

Conclusion:

noise-induced quantum coherence can enhance electron transport yield in photosynthetic complexes

SUMMARY

Quantum Coherence Can Improve Quantum Heat Engine (QHE) Efficiency

I. Quantum Thermodynamics

II. Photo-Carnot QHE

III. The Laser as a QHE

1. $$\frac{\hbar\nu_{laser}}{\hbar\nu_{pump}} = 1 - \frac{T_c}{T_h}$$ From Detailed Balance

2. Quantum Coherence Can Improve Laser QHE Quantum Efficiency by Breaking Detailed Balance

IV. The Photocell as a QHE

1. $$\frac{eV}{\hbar\nu_{pump}} = 1 - \frac{T_c}{T_h}$$ From Detailed Balance

2. Quantum Coherence Can Improve Photocell QHE Quantum Efficiency by Breaking Detailed Balance

V. Noise Induced Quantum Coherence Can Enhance:

1). Laser QHE Power

2). Photocell QHE Power

3). Efficiency of Photosynthesis

References

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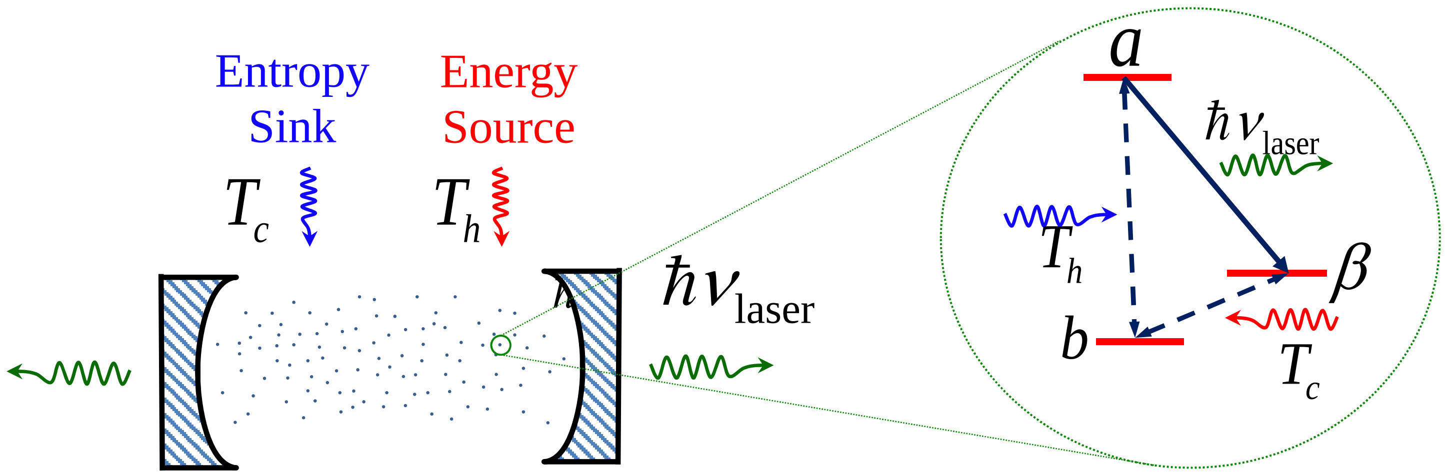
5. M.O. Scully, *Phys. Rev. Lett.* **104**:207701 (2010).
6. M.O. Scully, K.R. Chapin, K.E. Dorfman, M.B. Kim, A.A. Svidzinsky, *PNAS* **108**:15097 (2011).
7. K.E. Dorfman, D.V. Voronine, S. Mukamel, M.O. Scully, to be published.

Laser QHE

App I



$$\dot{\rho}_{bb} = \gamma_c[(1+\bar{n}_c)\rho_{\beta\beta} - \bar{n}_c\rho_{bb}] + \gamma_h[(1+\bar{n}_h)\rho_{aa} - \bar{n}_h\rho_{bb}]$$

$$\dot{\rho}_{\beta\beta} = \gamma_c[\bar{n}_c\rho_{bb} - (1+\bar{n}_c)\rho_{\beta\beta}] + \frac{P_l}{\hbar\nu_l}$$

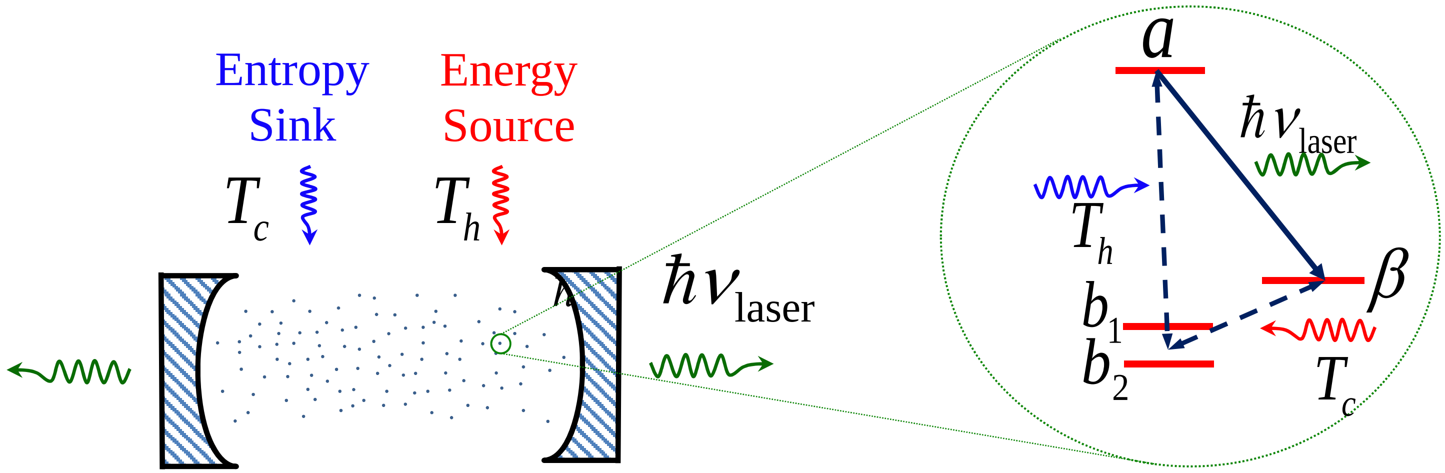
Laser power

$$\frac{P_l}{\hbar\nu_l} = \frac{g^2}{\gamma_l}(\rho_{aa} - \rho_{\beta\beta})\bar{n}_l$$

$$\rho_{aa} + \rho_{bb} + \rho_{\beta\beta} = 1$$

MOS, Chapin, Dorfman, Kim, and Svidzinsky, PNAS **108** 15097 (2011).

Laser QHE with noise induced coherence



$$\dot{\rho}_{11} = \gamma_{1c}[(1+\bar{n}_c)\rho_{\beta\beta} - \bar{n}_c\rho_{11}] + \gamma_{1h}[(1+\bar{n}_h)\rho_{aa} - \bar{n}_h\rho_{11}] -(\sqrt{\gamma_{1c}\gamma_{2c}}\bar{n}_c + \sqrt{\gamma_{1h}\gamma_{2h}}\bar{n}_h)Re[\rho_{12}]$$