### QUANTUM HEAT ENGINES AND QUANTUM COHERENCE EFFECTS IN SYSTEM-ENVIRONMENT INTERACTIONS





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## Outline

- Motivation: Quantum Heat Engines, quantum coherence and its detection
- Coherence enhanced laser, solar cell and photosynthetic QHE
- Efficiency at maximum power and quantum coherence



## What is quantum about QHE?



• Working fluid is quantum gas

#### What else can be quantum?

- Quantum thermal bath (molecular dynamics)
- Quantum effects in system-bath interactions (e.g. quantum coherence and interference)
- Quantum work (quantum radiation, backreaction)
- Quantum measurement (e.g. interaction free measurement)



Quantum coherence in physical and chemical systems

- Atomic systems EIT, LWI, CPT, etc.
- Heterostructures QCL
- Photosynthetic systems
- Chemical reactions (isomerization, e.g. rhodopsin)
- DNA repair
- Superexchange in electron transfer

In most of the above systems coherence is caused by the coupling between atomic (molecular) counterparts of the systems facilitating multiple interfering pathways for energy, electron and photon propagation. Coherence is relational (between system and environment)



## Quantum interference in quantum wells

Nature **390**, 589 (1997)

# Controlling the sign of quantum interference by tunnelling from quantum wells

Jérôme Faist\*, Federico Capasso, Carlo Sirtori\*, Ken W. West & L. N. Pfeiffer

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974-0636, USA





Applied Physics Letters 70, 3456 (1997)

Tunneling induced transparency: Fano interference in intersubband transitions

H. Schmidt,<sup>a)</sup> K. L. Campman, A. C. Gossard, and A. Imamoğlu Department of Electrical and Computer Engineering, University of California, Santa Barbara, California 93106





# Noise induded coherence and long-range charge separation



The dispersive lineshapes at short time are signatures of vibronic coherence present in the system,





## Quantifying Coherence via Lineshape analysis in Raman spectroscopy

Femtosecond Stimulated Raman Signals calculated using Stochastic Liouville Equation, *a* is the state after excitation

$$S_{FSRS}(\omega, T) = -\Im \frac{2}{\hbar} \mathcal{E}_{p}^{*}(\omega) |\mathcal{E}_{1}|^{2} \sum \alpha_{ad}^{2} \sum \mathcal{G}_{ad,ad,s}(\omega - \omega_{1})$$
$$\times \int_{-\infty}^{\infty} \frac{d\Delta}{2\pi} \mathcal{E}_{p}(\omega + \Delta) e^{i\Delta T} \rho_{aa}^{(s)}(-\Delta)$$

In the static limit (neglecting dynamics during dephasing)

$$S_{FSRS}(\omega,T) = \sum_{a} \sum_{s} S_{FSRS,a}^{(s)}(\omega) \rho_{aa}^{(s)}(T)$$

Absorptive (symmetric) lineshapes – long time dynamics

General case (coherence is prominent) – Fano (dispersive) lineshapes – short time dynamics

One can relate the degree of asymmetry to the microscopic molecular coherence

H.Ando, B.P. Fingerhut, K.E. Dorfman, J.D. Biggs, S. Mukamel, JACS 136, 14801 (2014); B. Agarwalla, H. Ando, K.E. Dorfman and S. Mukamel, JCP 142, 024115 (2015);





## Laser Quantum Heat Engine (QHE)

### PRL 2, 262 (1959) PHYSICAL REVIEW LETTERS

MARCH 15, 1959





Laser QHE



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

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

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

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

## Lasing without inversion



(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

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

O. Kocharovskaya, Phys. Rep. 219, 175 (1992);
S. Harris, Phys. Today 50, 36 (1997);
M. O. Scully and M. S. Zubairy, Quantum Optics (Cambridge University Press, Cambridge, UK, 1997).



#### Laser Oscillation without Population Inversion in a Sodium Atomic Beam

G. G. Padmabandu,<sup>1,2,\*</sup> George R. Welch,<sup>1,2</sup> Ivan N. Shubin,<sup>1</sup> Edward S. Fry,<sup>1,2,†</sup> Dmitri E. Nikonov,<sup>1,2,‡</sup> Mikhail D. Lukin,<sup>1,2</sup> and Marlan O. Scully<sup>1,2,3</sup> <sup>1</sup>Texas Laser Laboratory, Houston Advanced Research Center, The Woodlands, Texas 77381 <sup>2</sup>Department of Physics, Texas A&M University, College Station, Texas 77843-4242 <sup>3</sup>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  $\Lambda$  scheme within the sodium  $D_1$  line. This is also the first demonstration



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## P-n junction solar cells

3.5

GaN

4.0



- **1**. Photons with energy less then  $E_{q}$  are not absorbed
- 2. Thermal relaxation, energy is lost to phonons
- 3. Losses due to finite temperature of the cell (thermodynamic)



### Detailed balance Limit of Solar Cell Efficiency





- 30% efficient single-gap solar cell at one sun, for 1 e<sup>-</sup>/photon
- 44% ultimate efficiency

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

## Thermodynamic limit on solar cell efficiency



When electron goes from conduction band to valance band change in Helmholtz free energy (maximum work that can be extracted from the system) is

$$\Delta F = eV = E_g - T \Delta S \leftarrow \text{Change in entropy (losses)}$$
Change in  
internal energy Open circuit voltage
$$\eta_{\text{thermodynamic}} = \frac{eV_{oc}}{E_g}$$



#### Balance of radiative and absorption currents:



 $\varOmega_{\rm emit},\ \varOmega_{\rm Sun}$  - are solid angles of emitted radiation and the Sun viewed from the cell







### No light concentration:

$$\Omega_{\text{Sun}} = 6.8 \times 10^{-5}$$
,  $\Omega_{\text{emit}} = 4\pi$ ,  $E_g = 1.35 \text{ eV}$ :  $\eta_{\text{thermodynamic}} = 0.72$ 

## **Light concentration**



### **Full concentration:**

$$\Omega_{\text{sun}} = \Omega_{\text{emit}}: \eta_{\text{thermodynamic}} = 1 - \frac{T}{T_s} \leftarrow \text{Carnot efficiency}$$



## Photocell QHE



Current through the cell

$$j = e\Gamma \rho_{\alpha\alpha}$$

Voltage

P = jV

$$eV = E_{\alpha} - E_{\beta} + kT_c \ln\left(\frac{\rho_{\alpha\alpha}}{\rho_{\beta\beta}}\right)$$

Power delivered to the load

$$\begin{split} \dot{\rho}_{bb} &= \gamma_{v} \big[ (1 + \bar{n}_{v}) \rho_{\beta\beta} - \bar{n}_{v} \rho_{bb} \big] \\ &+ \gamma_{h} \big[ (1 + \bar{n}_{h}) \rho_{aa} - \bar{n}_{c} \rho_{bb} \big] \\ \dot{\rho}_{\beta\beta} &= -\gamma_{v} \big[ (1 + \bar{n}_{v}) \rho_{\beta\beta} - \bar{n}_{v} \rho_{bb} \big] + \frac{j}{e} \\ \dot{\rho}_{\alpha\alpha} &= -\gamma_{c} \big[ (1 + \bar{n}_{c}) \rho_{aa} - \bar{n}_{c} \rho_{\alpha\alpha} \big] - \frac{j}{e} \\ \rho_{aa} + \rho_{bb} + \rho_{\alpha\alpha} + \rho_{\beta\beta} = 1 \end{split}$$



## Quantum dot photo/solar cell



M. O. Scully, Phys. Rev. Lett. 104, 207701 (2010).



## Noise induced coherence. 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.





## Noise induced coherence. LWI

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#### So we can have coherence for free!



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

Optics Communications 281 (2008) 4940-4945

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

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



Steady state coherence

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



### QHE models with noise induced coherence



M.O. Scully, K.R. Chapin, K.E. Dorfman, M.B. Kim and A.A. Svidzinsky, PNAS 108, 15097 (2011)



## **Current-voltage characteristics**



#### Current and power are enhanced due to coherence



## Artificial vs Natural Light Harvesting



SCIENCE VOL 332 13 MAY 2011

# **Comparing Photosynthetic and Photovoltaic Efficiencies and Recognizing the Potential for Improvement**

Robert E. Blankenship,<sup>1\*</sup> David M. Tiede,<sup>2\*</sup> James Barber,<sup>3</sup> Gary W. Brudvig,<sup>4</sup> Graham Fleming,<sup>5</sup> Maria Ghirardi,<sup>6</sup> M. R. Gunner,<sup>7</sup> Wolfgang Junge,<sup>8</sup> David M. Kramer,<sup>9</sup> Anastasios Melis,<sup>10</sup> Thomas A. Moore,<sup>11</sup> Christopher C. Moser,<sup>12</sup> Daniel G. Nocera,<sup>13</sup> Arthur J. Nozik,<sup>14</sup> Donald R. Ort,<sup>15</sup> William W. Parson,<sup>16</sup> Roger C. Prince,<sup>17</sup> Richard T. Sayre<sup>18</sup>





## Primary process of photosynthesis

LETTERS

#### Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Vol 446 12 April 2007 doi:10.1038/nature05678

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



Sunlight absorbed by bacteriochlorophyll (green) within the FMO protein (gray) generates a wavelike motion of excitation energy whose quantum mechanical properties can be mapped through the use of two-dimensional electronic spectroscopy. (Image courtesy of Greg Engel, Lawrence Berkeley National Laboratory, Physical Biociences Division

Light harvesting in the antenna & charge separation in the reaction center  $\rightarrow$  remarkable, near unity quantum yield



#### What is the effect of coherence on charge separation?

Manifestation of coherence in various light harvesting complexes

Engel GS, et al. (2007) Nature 446:782–786. FMO (bacteria) Lee H, Cheng YC, Fleming GR (2007) Science 316:1462–1465. Bacteria reaction center Calhoun TR, et al. (2009) J Phys Chem B 113:16291–16295. LHII (plants) Collini E, et al. (2010) Nature 463:644–647. Algae



## Photosynthetic Quantum Heat Engine

### This model looks like a model of coherence enhanced solar cell



Reaction center (primary charge separation)



### Parameter regimes





Noise induced coherence is responsible for: oscillatory population dynamics and enhancement of the charge separation efficiency

K.E. Dorfman, D.V. Voronine, S. Mukamel and M.O. Scully PNAS 110, 2746 (2013)



## The power enhancement demonstrated for a given model of QHE corresponds to very low efficiency regime.

Is there any effect of the coherence on the efficiency at maximum power?



## Heat and Work

Markovian master equationDissipator $\dot{\rho} = \mathcal{L}[\rho] = \mathcal{L}_h[\rho] + \mathcal{L}_d[\rho]$  $\mathcal{L}_h[\rho] = -(i/\hbar)[H(t), \rho]$  $\mathcal{L}_d[\rho]$ Average energyHeatWork $\langle E \rangle = \operatorname{Tr}\{\rho(t)H(t)\}$  $Q = \int_0^t \operatorname{Tr}\left\{\frac{d\rho(t')}{dt'}H(t')\right\}dt'$  $W = \int_0^t \operatorname{Tr}\left\{\rho(t')\frac{dH(t')}{dt'}\right\}dt'$ Spohn entropy (nonnegative for e.g. Lindbladt dissipator)Steady state $\sigma = \frac{\partial S}{\partial t} - \frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_C}{T_C}$  $S = -k_B \operatorname{Tr}\{\rho \ln(\rho)\}$  $\partial S/\partial t = 0$ 

 $\begin{array}{ll} \mbox{Heat flux} & \mbox{Energy flux} \\ \dot{Q}_{H(C)} = \mbox{Tr} \{ \mathcal{L}_{dH(C)}[\rho]H \} & \mbox{\dot{E}}_0 = \dot{Q}_{H0} + \dot{Q}_{C0} + P_0 & \mbox{P=dW/dt} \\ \mbox{Two contributions} & \mbox{If} & \dot{Q}_{C(H)V} = 0 \\ \dot{Q}_{H(C)} = \dot{Q}_{H(C)0} + \dot{Q}_{H(C)V} & \\ \dot{Q}_{H(C)V} = \mbox{Tr} \{ \mathcal{L}_{dH(C)}[\rho]V \} & \mbox{\eta} \equiv -\frac{P_0}{\dot{Q}_{H0}} \leq \frac{T_H - T_C}{T_H} \end{array}$ 

R. Alicki, J. Phys. A 12, L103 (1979)



## Efficiency at maximum power Chambadal-Novikov-Curzon-Ahlborn limit



Efficiency of a 3-level QHE

$$\eta = 1 - \frac{\omega_c}{\omega_h}$$

Power of a 3-level QHE at high T limit

$$P = A(\omega_h - \omega_c) \left(\frac{T_h}{\omega_h} - \frac{T_c}{\omega_c}\right)$$

Optimization of the power

$$\frac{\omega_c}{\omega_b} = \sqrt{\frac{T_c}{T_b}}$$

Curzon-Ahlborn efficiency

$$\eta_{\rm CA} = 1 - \sqrt{\frac{T_c}{T_b}},$$

R. Kosloff, A. Levy, Annu. Rev. Phys. Chem. 65, 365 (2014); I. Novikov, (1957), P. Chambadal (1957), Curzon, Ahlborn (1975).



## Efficiency at maximum power of low-dissipation **Carnot engines**



$$\frac{\Sigma_h/\tau_h - T_c \Sigma_c/\tau_c}{\tau_c} \qquad \qquad \frac{\eta_C}{2} \equiv \eta_- \leq \eta^* \leq \eta_+ \equiv \frac{\eta_C}{2 - \eta_C}$$

M. Esposito, R. Kawai, K. Lindenberg, C. Van den Broeck, Phys. Rev. Lett. 105, 150603 (2010)



#### Efficiency at maximum power for Scovil Schulz-Dubois (SSD) model



Power

 $P = -i \operatorname{Tr}([H_0, V_R]\rho_R)$ 

Equivalent to quantum calculation for the photon number

 $\dot{Q}_h = \operatorname{Tr}(\mathcal{L}_h[\rho_R]H_0)$ 

Heat flux

Laser-matter interaction

$$V(t) = \hbar \lambda (e^{i\omega t} |1\rangle \langle 0| + e^{-i\omega t} |0\rangle \langle 1|).$$

Strong coupling to the laser field  $\lambda \gg \Gamma_h, \Gamma_c$ 

Hot bath Liouvillian

$$\mathcal{L}_{h}[\rho] = \Gamma_{h}(n_{h}+1)[2|g\rangle\langle g|\rho_{11}-|1\rangle\langle 1|\rho-\rho|1\rangle\langle 1|] + \Gamma_{h}n_{h}[2|1\rangle\langle 1|\rho_{gg}-|g\rangle\langle g|\rho-\rho|g\rangle\langle g|]$$

Efficiency  $\eta = -\frac{P}{\dot{Q}_h} \qquad \qquad \eta = 1 - \frac{\omega_c}{\omega_h}$ 

E. Boukobza, D.J. Tannor, PRA 74, 063822 (2006); PRL 98, 240601 (2007)



## Efficiency at maximum power

Fixing 
$$\omega_{\rm h}$$
 while varying  $\omega_{\rm c}$   

$$\eta^{(\omega_h)}(P_{\rm max}) = 1 - \frac{\sqrt{(1+r)(1-\eta_C)(1+r-\eta_C)} - (1-\eta_C)}{r} \qquad r = \Gamma_h/\Gamma_c$$

Fixing  $\omega_c$  while varying  $\omega_h$ 

$$\eta^{(\omega_c)}(P_{\max}) = 1 - \frac{1 - \eta_C}{\sqrt{(1+r)(1+r - \eta_C)} - r}$$

Limiting cases

$$r \to 0 \qquad r \to \infty$$
  
$$\eta_C/2 < \eta^{(\omega_h)}(P_{\max}) < \eta_{CA}$$
  
$$\eta_{CA} < \eta^{(\omega_c)}(P_{\max}) < \eta_C/(2 - \eta_C)$$







## **Coherence effects**

Laser radiation is coupled to both upper levels

 $V(t) = \hbar\lambda(e^{i\omega t}(|1\rangle\langle 0| + |2\rangle\langle 0|) + e^{-i\omega t}(|0\rangle\langle 1| + |0\rangle\langle 2|))$ 

Efficiency is dependent upon density matrix (symmetry breaking)

$$\eta_Q = 1 - \frac{\omega_c}{\omega_h + \Delta\xi} \qquad \xi = \frac{\rho_{01} - \rho_{10} - \rho_{02} + \rho_{20}}{\rho_{01} - \rho_{10} + \rho_{02} - \rho_{20}}$$

If  $\Delta \xi > 0$  does it mean we can get more than CA efficiency? If  $\Delta$ =0 does it mean we get the same answer as in SSD?

Similarly the heat bath is governed by generalized Lindblad (interference terms)

$$\dot{\rho}_{10} = -[i(\omega_{10} - \omega) + \Gamma_c(n_c + 1) + \Gamma_{h1}(n_{h1} + 1)]\rho_{10} + i\lambda(\rho_{11} - \rho_{00} + \rho_{12}) - p\sqrt{\Gamma_{h1}\Gamma_{h2}}(n_{h2} + 1)\rho_{20},$$

p=1 constructive interference, p=-1 destructive interference, p=0 no interference



## Efficiency with coherence (degenerate levels)



Coherence effect



Nondegenerate case does not improve the efficiency. Symmetry is not broken (result does not depend on the sign of  $\Gamma_{h1}$ - $\Gamma_{h2}$ 



## Low temperature operation

Fixing  $\omega_{\rm h}$  while varying  $\omega_{\rm c}$  $\eta^{(\omega_h)}(P_{\rm max}) = \frac{1 - \eta_C}{N_h} \left[ \operatorname{Plog}\left( e^{1 + \frac{N_h \eta_C}{1 - \eta_C}} \right) - 1 \right]$ 

Fixing  $\omega_c$  while varying  $\omega_h$ 

$$\eta^{(\omega_c)}(P_{\max}) = 1 - \frac{N_c(1 - \eta_C)}{1 + N_c(1 - \eta_C) + \text{Plog}(e^{1 - N_c \eta_C})}$$

$$\eta_C/2 < \eta^{(\omega_h)} < \eta_C$$

$$\frac{P_{\max}(p \neq 0)}{P_{\max}(p = 0)} = \frac{r+1}{r + \frac{1}{1+p}} \to (p \to 1) \simeq 1/2$$

Plog is a product log function which is a principal solution for w in  $z=we^{w}$ ,  $N_c=\omega_c/T_c>>1$ ,  $N_h=\omega_h/T_h>>1$ . No dependence upon coherence!



Degenerate case does not depend on the rate of spontaneous emission - reversible limit (see e.g. S.E. Harris, PRA 94, 053859 (2016))



## Summary

- Efficiency at maximum power for Scovil Schulz-DuBois maser lies within the same boundary as for more general finite time Carnot engines without additional assumptions on the relation between dissipation and relaxation times.
- Bath (noise) induced coherence may enhance power output of the photosynthetic, photovoltaic and laser QHE.
- Present results demonstrate the effects of quantum interference on efficiency at maximum power (practical limit for efficiency)
- Weak coupling to the bath yields few percent effect on the coherence enhanced efficiency at maximum power (weak coupling – weak effect)
- For degenerate coupled states at low temperature coherence does not play role.



## **Collaborators:**



Jianshu Cao



Dazhi Xu



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