Relevance of incoherent light-induced coherences for photosynthetic energy transfer

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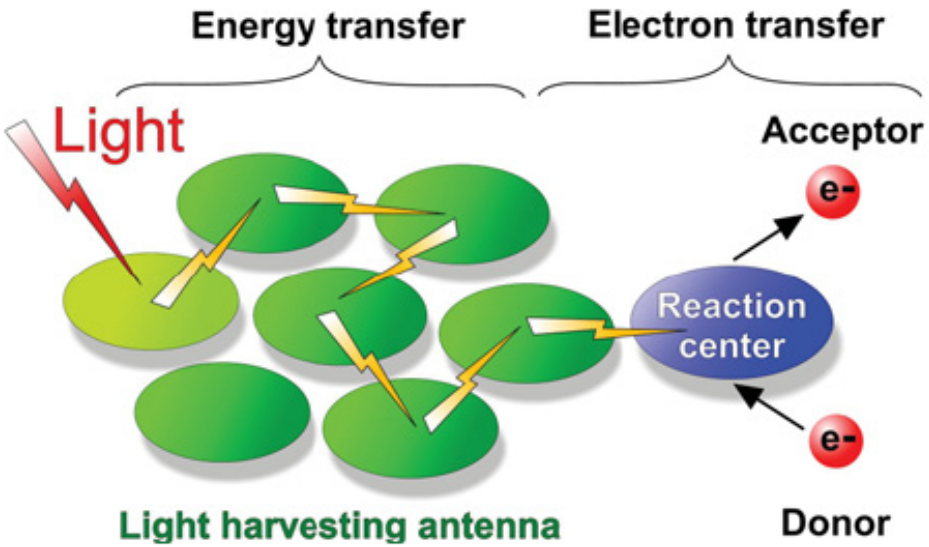
Photosynthetic energy transfer

- central **physical process** during the **primary steps** of natural photosynthesis
- LH antenna = pigments (e.g. chlorophyll) + protein matrix

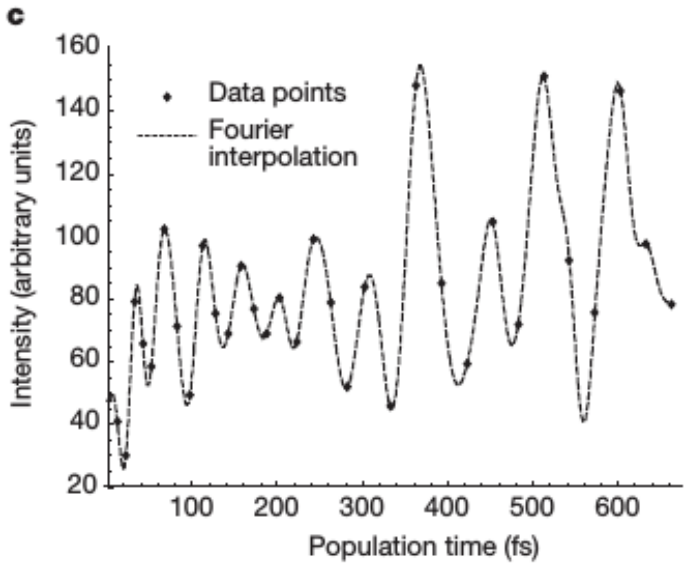


1. **light absorption** and **energy transfer (transport of Frenkel excitons)** in antenna;
   energy delivery to the reaction center (RC)
2. primary electron transfer in the RC
3. energy stabilization by a redox cascade (electron transport)
4. synthesis and export of stable products

The dawn of quantum biology: Nature **446**, 782 ('07)

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]



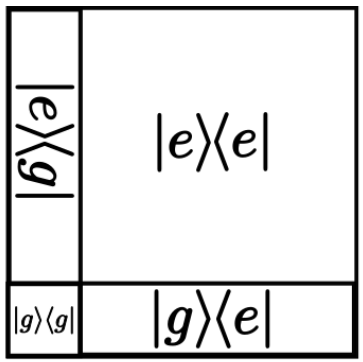
- 2D FT ES
- oscillations persist for at least 660 fs
- theory predicts ∼50 fs
- everything happens in the "warm, wet and noisy environment"
- origin of coherences observed?
- how do they persist?
- coherences and evolution?

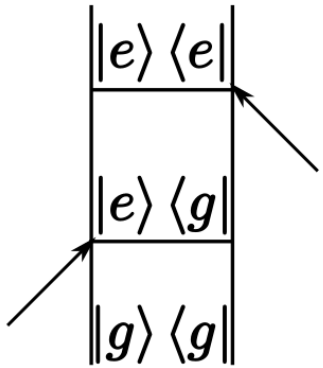
Questions that we address

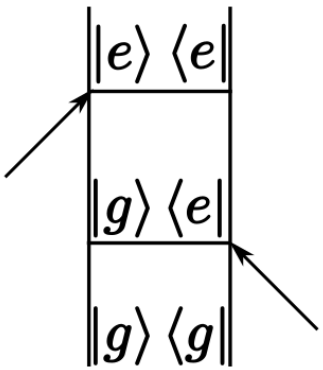
- expt. signal $\leftrightarrow$ nonlinear polarization $P^{(3)}$
  - theoretical nonlinear spectroscopy
- the state of an initially unexcited antenna under different excitation conditions (weak excitation)?
  - density matrix theory including the photoexcitation step
  - interaction with the environment may not be weak, reorganization processes may not be fast
    - Redfield and Förster may not work
  - excitation by pulsed coherent light (in laboratories)
    - $\left\langle E^{(-)}(\tau_2)E^{(+)}(\tau_1)\right\rangle_R = \underbrace{\left\langle E^{(-)}(\tau_2)\right\rangle_R \left\langle E^{(+)}(\tau_1)\right\rangle_R}_{\text{single-particle part}\atop\text{classical factorization}}$
  - excitation by continuous incoherent light (in Nature)
    - $\left\langle E^{(-)}(\tau_2)E^{(+)}(\tau_1)\right\rangle_R = \underbrace{\delta\left\langle E^{(-)}(\tau_2)E^{(+)}(\tau_1)\right\rangle_R}_{\text{two-particle correlations}\atop\text{quantum fluctuations}}$

Exact excitonic dynamics under driving

- second-order treatment of the interaction with light
- exact treatment of the exciton–environment interaction
  - generalization of the Feynman–Vernon influence functional theory for systems subjected to weak driving







$$\rho_{ee}^{(I)}(t) = \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \left(\vec{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) A_{ee}^{(I)}(\tau_2,\tau_1) + A_{ee}^{(I)\dagger}(\tau_2,\tau_1) \overleftarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) \right)$$

$$\rho_{eg}^{(I)}(t) = \int_{t_0}^{t} d\tau \, \vec{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,t,\tau) A_{eg}^{(I)}(\tau)$$

$$A_{ee}^{(I)}(\tau_2,\tau_1) = \frac{1}{\hbar^2} \sum_{i,j} \mu_{eg,j}^{(I)}(\tau_1) G_{ij}^{(1)}(\tau_2,\tau_1) \mu_{ge,i}^{(I)}(\tau_2)$$

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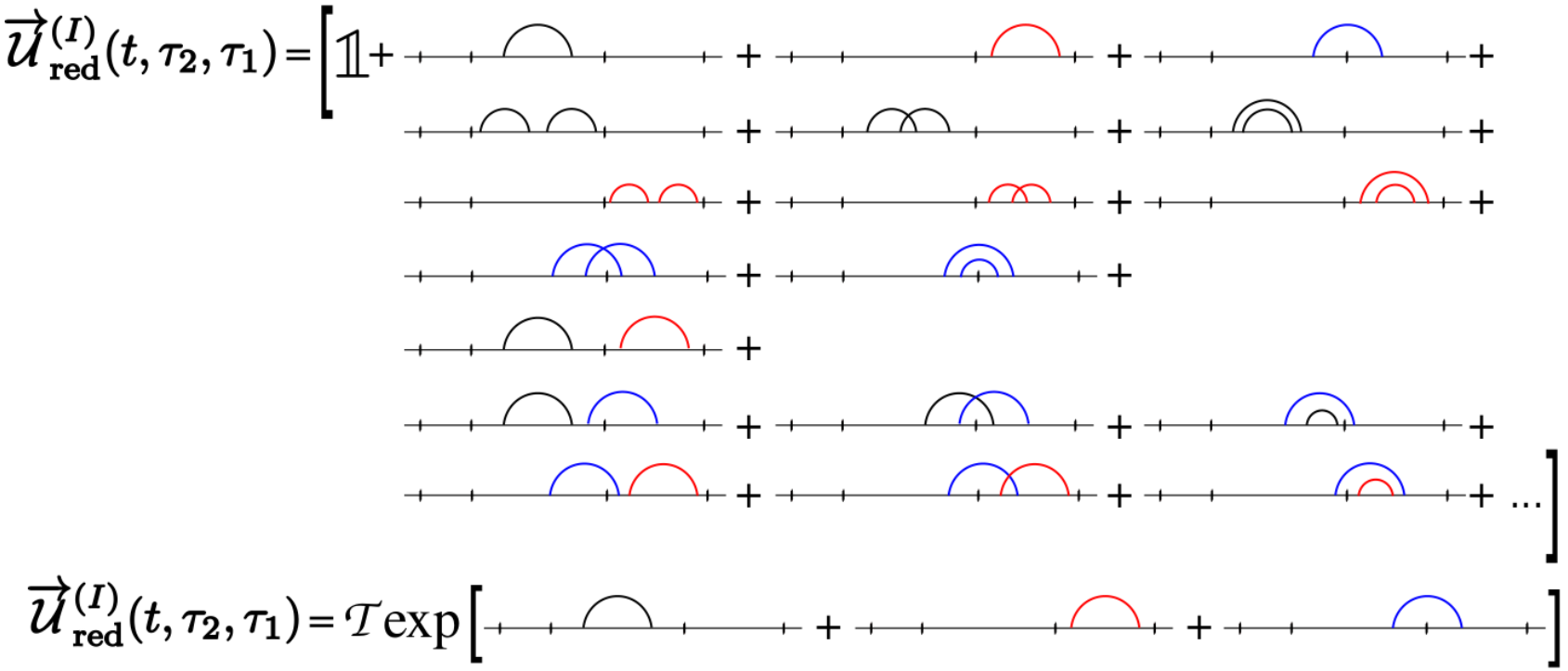
Novelty: Exact evolution superoperator



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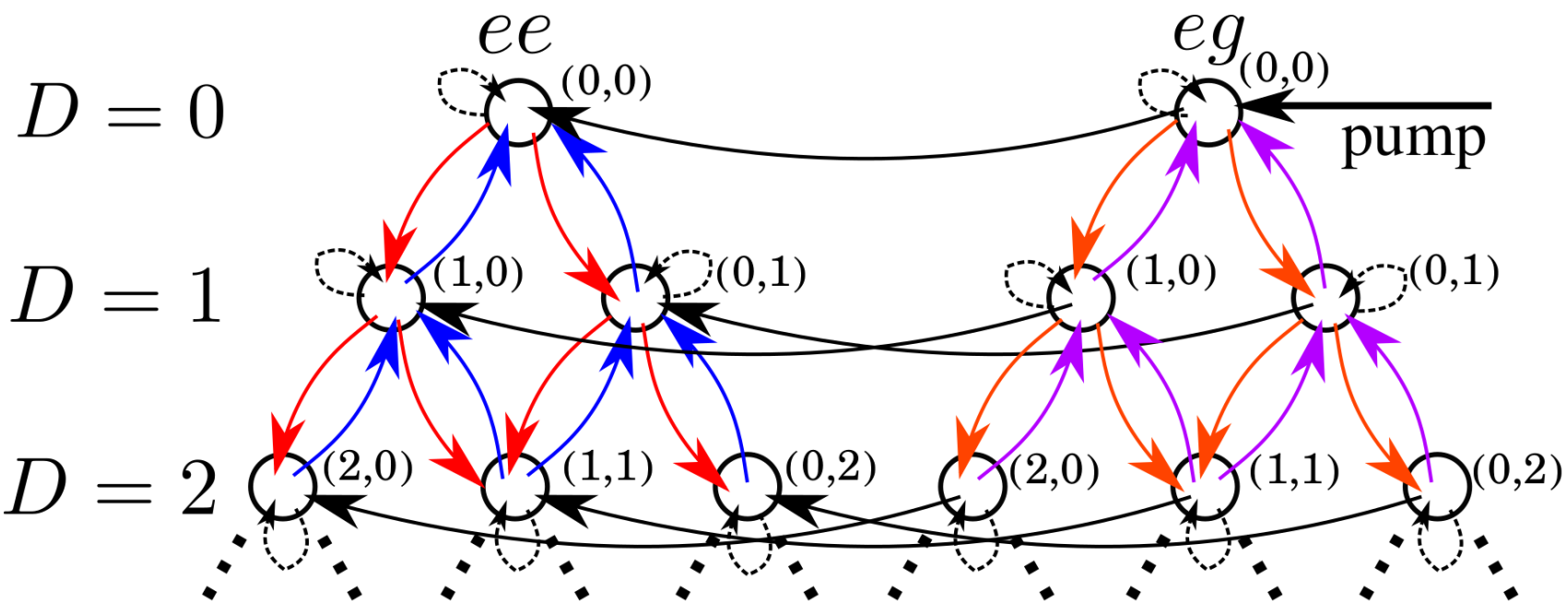
- phonon-assisted processes of an arbitrary order
- circumferences represent $C_j(s_2 - s_1)$
- straddling diagram (phonon assistance starts in eg, and ends in ee)

Novelty: HEOM + photoexcitation

- one usually solved the ee sector only (ultrafast excitation)
- solving the eg sector is simpler (one-sided objects, WF-like)
- valid for both coherent and incoherent light
- may be solved in any basis (local, excitonic, etc.)



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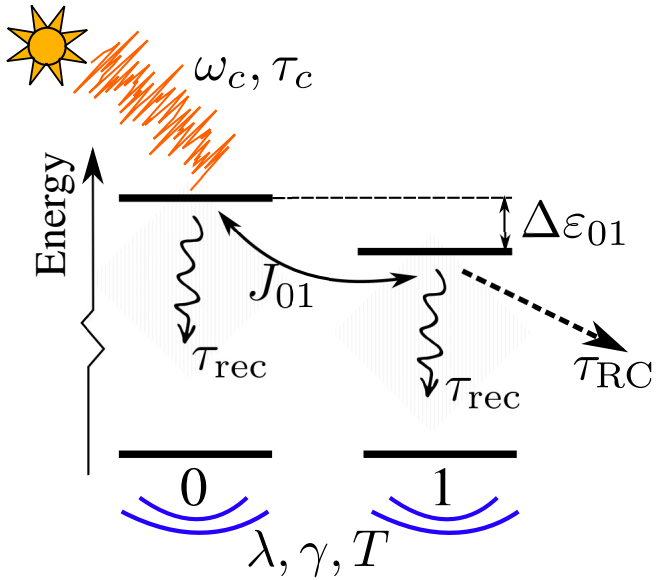
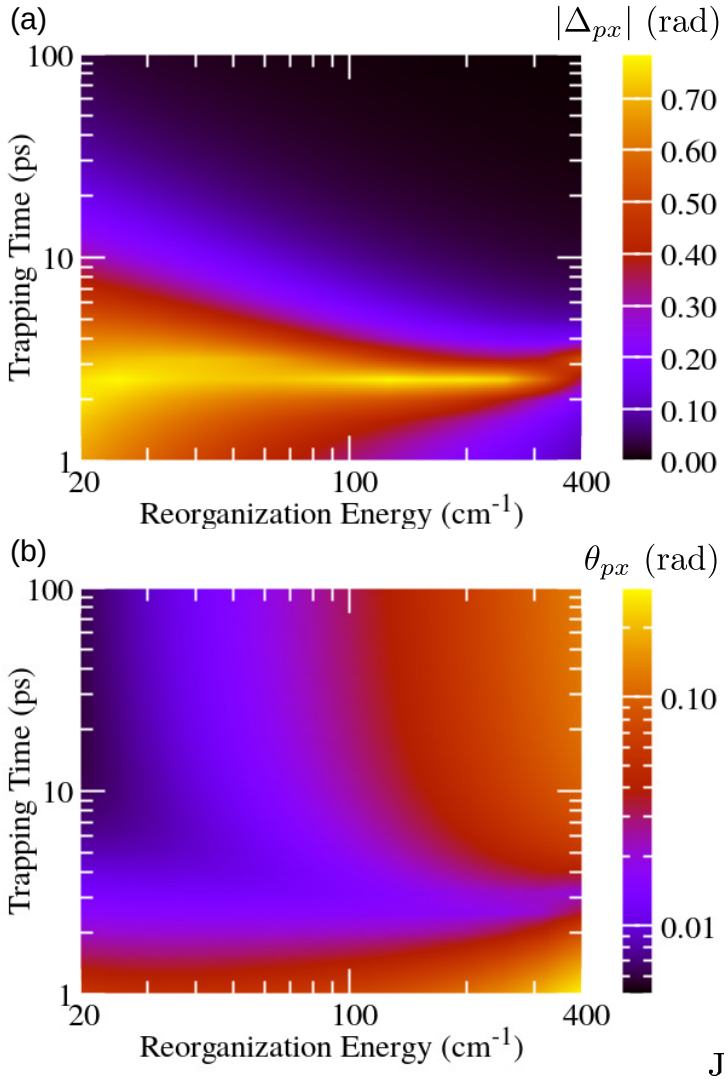
Asymmetric photosynthetic dimer and preferred basis



- V-type system
- incoherent (chaotic) light
- recombination
- delivery to the RC
- iterative procedure to solve for the steady state ρ^{ss}

- $\langle \widehat{M} \rangle^{ss} = \mathrm{Tr}_M\{\widehat{M}\rho^{ss}\}$
- the basis in which $\langle \widehat{M} \rangle^{ss}$ is most naturally computed is the eigenbasis of ρ^{ss}
  - **the preferred basis**
- steady-state coherences can be eliminated from $\langle \widehat{M} \rangle^{ss}$
- factors determining preferred basis
  1. generation
  2. energy relaxation
  3. recombination
  4. extraction at RC

Excitonic basis ↔ preferred basis



$$\begin{pmatrix} |p_0\rangle \\ |p_1\rangle \end{pmatrix} = e^{i\varphi_{px}/2} \begin{pmatrix} e^{i\psi_{px}} & 0 \\ 0 & e^{-i\psi_{px}} \end{pmatrix} \times \begin{pmatrix} \cos\theta_{px} & \sin\theta_{px} \\ -\sin\theta_{px} & \cos\theta_{px} \end{pmatrix} \times \begin{pmatrix} e^{i\Delta_{px}} & 0 \\ 0 & e^{-i\Delta_{px}} \end{pmatrix} \begin{pmatrix} |x_0\rangle \\ |x_1\rangle \end{pmatrix}$$

- slow delivery ($\tau_{\mathrm{RC}} \gtrsim 20$ ps)
  - $\Delta_{px} \to 0$
  - θ_{px} originates from the excitation–environment entanglement
- fast delivery?

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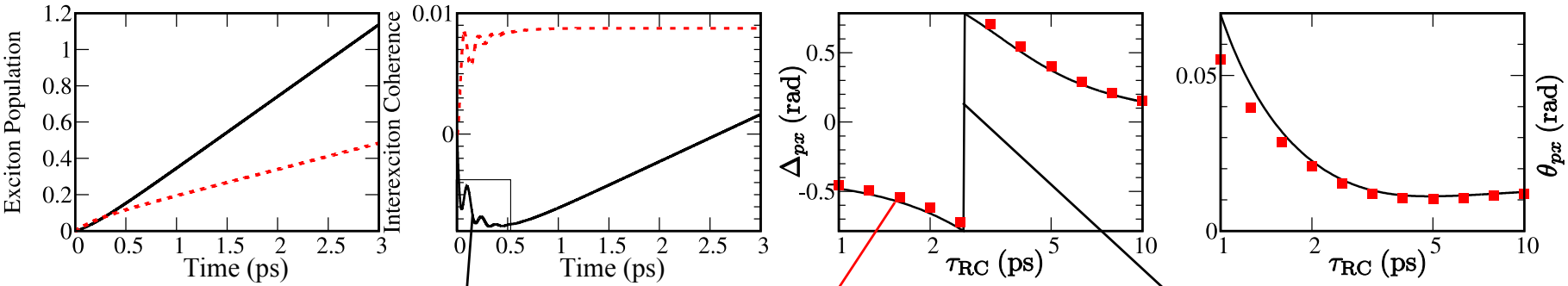
Relation between time-dependent and stationary picture

time evolution
incoherently driven
initially unexcited
unloaded (no rec, no RC)

$$\rho^{\mathrm{ul}}(\tau_{\mathrm{RC}}) \sim \rho^{ss}$$

steady state
incoherently driven
initially unexcited
loaded (rec, RC)



ultrafast beatings

from time-dependent data
extracted at $t = \tau_{\mathrm{RC}}$

from steady-state data

- crucial: the hierarchy of time scales
  - $\tau_{\mathrm{ET}} \ll \tau_{\mathrm{RC}} \lll \tau_{\mathrm{rec}}$

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Epilogue

- we formulate an exact description of excitonic dynamics in molecular aggregates weakly driven by light of arbitrary properties
- we examine the state in which the aggregate finds itself when subjected to continuous driving, excitation delivery, and recombination
- steady-state electronic coherences can be eliminated by transferring to the preferred basis
- slow delivery: like in unloaded aggregate, the interaction with the bath singles out the preferred basis
- fast delivery: relation between time-dependent and stationary picture
  - ultrafast experiments are important because they tell us about τ_{ET} and determine minimal τ_{RC} above which ultrafast artifacts are unimporant

Collaborators, Funding, Papers

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- papers
  - Janković and Mančal, J. Chem. Phys. **153**, 244110 ('20).
  - Janković and Mančal, J. Chem. Phys. **153**, 244122 ('20).