Coherence and dissipation in photosynthetic energy transfer

Tobias Kramer

Zuse Institute Berlin
Department of Physics, Harvard University

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Quantum-classical transition in many-body systems:
Indistinguishability, Interference and Interactions

QUANTUM $\to$ CLASSICAL WORLD $(\to)$ QUANTUM

Some remarks about “quantum” vs “classical” effects:

- classical transport equations arise from performing the limit $\hbar \to \mathbf{0}$
- to overcome the highly oscillatory behaviour of this limit:
  some smearing (spatially, energetically) required
- to invent and program a classical **ERSATZ** system to perform a “quantum dynamics” does not imply there are no quantum effects in the quantum system (fractional quantum Hall effect = classical plasma)
- semiclassics explores similarities of classical and quantum dynamics:
  replace operators by mean values (coherent states), or
  path integrals by stationary phase value (scattering, transport)
- possible advantage of semiclassics: cheaper computational method, but might require ensemble averages.

Where does this put energy transfer in photosynthesis?

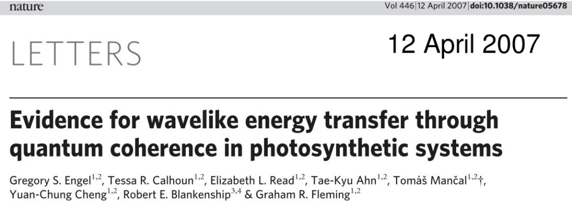
OUTLINE OF THE PRESENTATION

1. Green sulfur bacteria: the most primitive system well characterized
2. experimental observations and theoretical tools for interpretation
3. quantum dynamics in dissipative environments
4. conclusions

FMO: The bacteria forgotten in the fridge…

Olson, *The FMO protein*,
Photos. Res. **80** 181 (2004)

> In 1964 my assistant, Frances Roskosky, had accidentally crystallized the BChl a protein by concentrating a solution almost to dryness and leaving it in the refrigerator. Patricia Cole (summer student) spent the summer of 1966 growing crystals up to 1mm long and 0.3mm wide in anticipation of future X-ray crystallography.



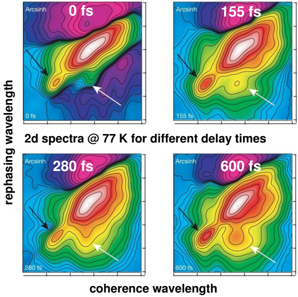
nature Vol 446|12 April 2007|**doi:10.1038/nature05678**

LETTERS

12 April 2007

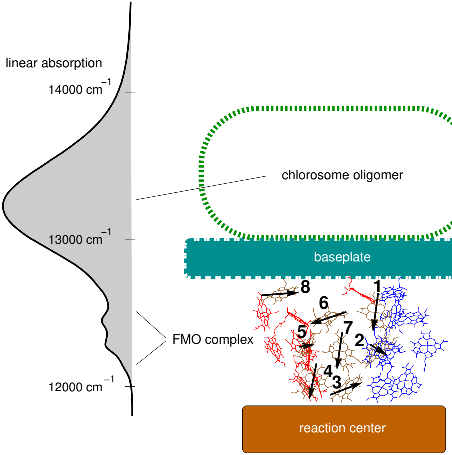
Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

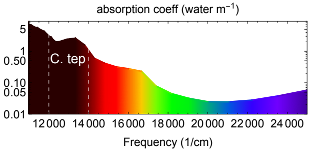
Gregory S. Engel[1,2], Tessa R. Calhoun[1,2], Elizabeth L. Read[1,2], Tae-Kyu Ahn[1,2], Tomáš Mančal[1,2]†, Yuan-Chung Cheng[1,2], Robert E. Blankenship[3,4] & Graham R. Fleming[1,2]



2d spectra @ 77 K for different delay times

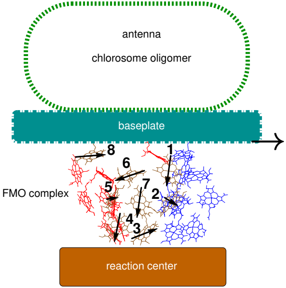
ENERGY TRANSFER CHAIN IN *Chlorobium tepidum*





1. proteins stabilize and tune pigments (“chlorophylls”)
2. light is absorbed by antenna, creates excited state
3. excitation is transferred to neighbouring pigments and channeled to the reaction center (ca 100-5000 pigments deliver to one reaction center). Purpose: maintain high rate of energy transfer even in low-light conditions
4. plants: in case of too much light, excess energy quenched

EXCITON HAMILTONIAN OF *C. tepidum*



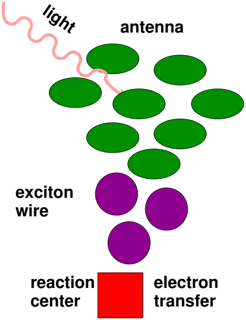
$$\begin{pmatrix} 13250 & 3 & 0 & 0 & 0 & 0 & 3 & 0 \\ 3 & 12410 & -87 & 5 & -5 & 6 & -13 & -9 \\ 0 & -87 & 12530 & 30 & 8 & 1 & 11 & 4 \\ 0 & 5 & 30 & 12210 & -53 & -2 & -9 & 6 \\ 0 & -5 & 8 & -53 & 12320 & -70 & -17 & -63 \\ 0 & 6 & 1 & -2 & -70 & 12480 & 81 & -1 \\ 3 & -13 & 11 & -9 & -17 & 81 & 12630 & 39 \\ 0 & -9 & 4 & 6 & -63 & -1 & 39 & 12440 \end{pmatrix} \mathrm{cm}^{-1}$$

ADOLPHS & RENGER Biophys J (2006)
TK & RODRÍGUEZ Sci Rep (2017)

exciton Hamiltonian ⟶ open quantum system (CALDEIRA & LEGGETT)

$$\mathcal{H} = \underbrace{\sum_{m=1}^{7} \varepsilon_m |m\rangle\langle m| + \sum_{m>n} J_{mn}\left(|m\rangle\langle n| + |n\rangle\langle m|\right)}_{\text{exciton dynamics}} + \underbrace{\sum_{m,i} |m\rangle\langle m| \lambda_i \left(b_{i,m}^{\dagger} + b_{i,m}\right) + \sum_{m,i} \hbar\omega_i b_i^{\dagger} b_i}_{\text{vibrational coupling}}$$

THEORETICAL MODEL: RATE EQUATIONS



Excitonic from antenna to reaction center via $\boldsymbol{M}$ sites: rate equation for population transfer[1]

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{ii}(t) = \sum_{m}^{M} \rho_{mm}(t) \cdot k_{mi} - \rho_{ii}(t) \sum_{m}^{M} k_{im}$$

Rates k_{mi} temperature T dependent, given by Foerster resonant energy-transfer for network Hamiltonian $\mathcal{H}$

Time-dependent t solution by exponentiation:

$$\rho(t) = \rho(0)\exp[kt], \quad \rho(\infty) = \frac{\mathrm{e}^{-\mathcal{H}/(k_B T)}}{\mathrm{Tr}\,\mathrm{e}^{-\mathcal{H}/(k_B T)}}$$

Easily solvable by matrix diagonalization.
No oscillatory behaviour, long-time thermal state.

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[1] PEARLSTEIN, Photochem Photobiol, 1982, **35**, 835

FROM “CLASSICAL” RATES TO QUANTUM DYNAMICS

	Big energy gap	Coherence between sites	Coherence between exciton states	Population-coherence transfers	Weakly coupled isoenergetic sites	Realistic line shape	Realistic spectral density	Reorganization	Computational time
Secular Redfield	—	✓	✓	—	—	—	✓	—	short
Full Refield	—	✓	✓	✓	✓	—	✓	—	short
Mod. Redfield	✓	✓	—	—	—	✓	✓	—	short
Förster	✓	—	—	—	✓	✓	✓	—	short
Std HEOM	✓	✓	✓	✓	✓	✓	—	✓	long
GPU-HEOM[1]	✓	✓	✓	✓	✓	✓	✓	✓	short

QM Density matrix approach

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{\text{excitons}}(t) = -\mathrm{i}\,\mathrm{Tr}_{\text{vibrations}}\left[\mathcal{H},\rho(t)\right]$$

- ☹ not a closed expression for reduced (electronic) density matrix
- ☹ perturbation expansion fails for photosynthetic systems: thermal energy ∼ energy gap ∼ coupling to vibrations
- ☹ large reorganization energies leading to significant shifts of the energy landscape, $|\textit{vibrations}\rangle \otimes |\textbf{excitons}\rangle$ not separable

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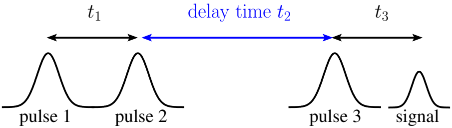
[1] Kreisbeck, TK, Hein, Rodríguez *High-Performance Solution of Hierarchical Equations of Motion for Studying Energy Transfer in Light-Harvesting Complexes*, J Chem Theory Comput (2011)

Time-resolved spectroscopy (2DES)

Excitation with several pulses can populate two excitons

$$\boldsymbol{H}_{\text{exciton}} = \begin{pmatrix} \boldsymbol{H}_{0\text{ exciton}} & & \\ & \boldsymbol{H}_{1\text{ exciton}} & \\ & & \boldsymbol{H}_{2\text{ excitons}} \end{pmatrix}$$

3 probe pulses sent in, one outgoing signal pulse recorded, phase matching either rephasing $\boldsymbol{k}^{RP}_{\text{signal}} = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$ or non-rephasing $\boldsymbol{k}^{NR}_{\text{signal}} = \boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$

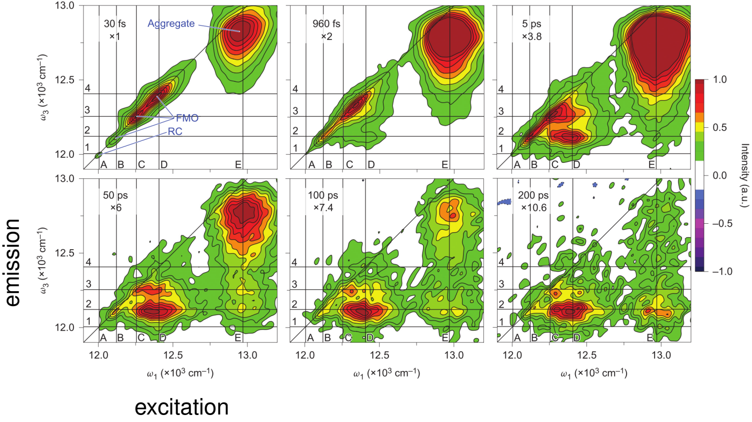


Compute 3rd order response function from dipole $\boldsymbol{\mu}(\boldsymbol{t})$ correlations:

$$\boldsymbol{S}(\omega_3; t_2; \omega_1) = \int_0^\infty \mathrm{d}t_1 \int_0^\infty \mathrm{d}t_3 \; \mathrm{e}^{\mathrm{i}(-t_1\omega_1 + t_3\omega_3)} \mathrm{Tr}\Big(\underbrace{\hat{\mu}(t_3 + t_2 + t_1)}_{\text{signal}} \Big[\underbrace{\hat{\mu}(t_2 + t_1)}_{\text{pulse 3}}, \Big[\underbrace{\mu(t_1)}_{\text{pulse 2}}, \Big[\underbrace{\hat{\mu}(0)}_{\text{pulse 1}}, \rho_0 \Big]\Big]\Big]\Big)$$

TRACKING THE EXCITATION ENERGY FLOW (EXP)

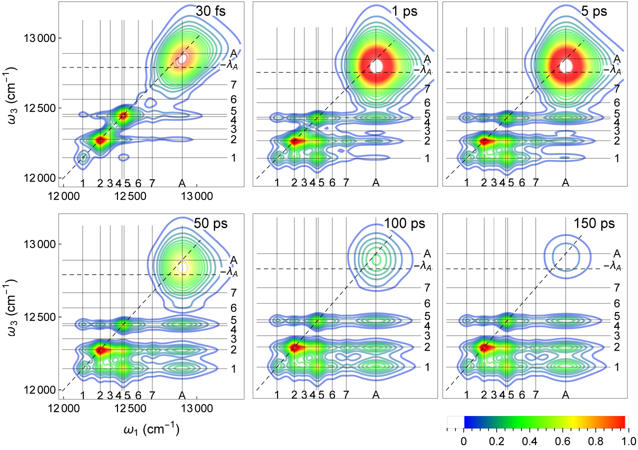
Measurement of the exciton flow in *C. tepidum*



DOSTÁL, PŠENČÍK, & ZIGMANTAS, Nat Chem 2016

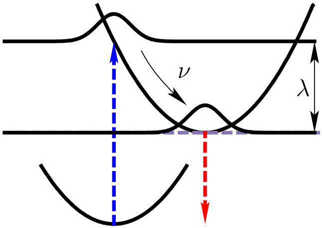
TRACKING THE EXCITATION ENERGY FLOW (THEO)

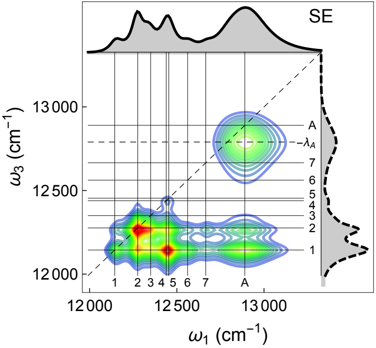
Simulation of the exciton flow in *C. tepidum* (GPU-HEOM)



TK & RODRÍGUEZ, Sci Rep 2017

REORGANIZATION SHIFTS





- time-dependent reorganization shifts handled by HEOM
- large reorg energy $\boldsymbol{\lambda}$ leads to entangled $|\textit{\textbf{vibrations}}\rangle \otimes |\textbf{excitons}\rangle$
- optimality of energy transfer depends critically on $\boldsymbol{\lambda}$

HIERARCHICAL EQUATIONS OF MOTION (HEOM)

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = -\frac{\mathrm{i}}{\hbar}\underbrace{[\mathcal{H},\rho(t)]}_{\text{coherent dynamics}} + \sum_{m=1}^{d}\underbrace{\mathrm{i}V^{\times}_{\text{m,vibr}}\sigma^{P_m\{1,\dots,0\}}(t)}_{\text{coupling to vibrations}}$$

millions of auxiliary density matrices $\sigma^{(n_1,\dots,n_d)}(t)$ store vibrational state

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma^{(n_1,\dots,n_d)}(t) = -\frac{\mathrm{i}}{\hbar}\overbrace{[\mathcal{H},\sigma^{(n_1,\dots,n_d)}(t)]}^{\text{small matrix} \times \text{small matrices (aligned)}} + \sum_{m=1}^{d} n_m\gamma\sigma^{(n_1,\dots,n_d)}(t)$$

$$+\sum_{m=1}^{d}\mathrm{i}\,\overbrace{V^{\times}_{\text{m,vibr}}\sigma^{(n_1,\dots,n_m+1,\dots,n_d)}(t)}^{\text{small matrix} \times \text{small matrix (jumps)}} + \sum_{m=1}^{d} n_m\,\overbrace{\theta_m(\gamma)\sigma^{(n_1,\dots,n_m-1,\dots,n_d)}(t)}^{\text{small matrix} \times \text{small matrix (jumps)}}$$

- dissipative vibrational mode density $J(\omega) = \frac{2\gamma\lambda\omega}{\gamma^2+\omega^2}$
- hierarchy truncated at $N_{\text{max}} = \sum_{m=1}^{d} n_m$ (typical $N_{\text{max}} \sim 3$, 100,000 equations)

- GPU-HEOM adaption and extension to different spectral density

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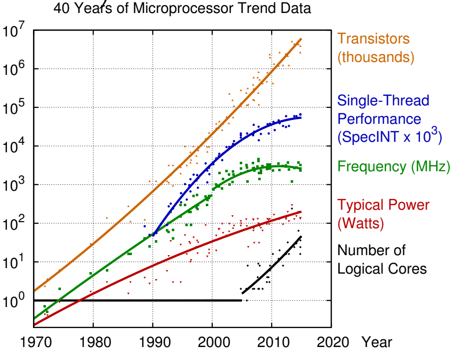
TANIMURA, KUBO J Phys Soc Jpn **58**, 101 (1989); ISHIZAKI, FLEMING J Chem Phys **130**, 234111 (2009)

KREISBECK, TK, HEIN, RODRÍGUEZ *High-Performance Solution of Hierarchical Equations of Motion for Studying Energy Transfer in Light-Harvesting Complexes*, J Chem Theory Comput **7**, (2011)

(QUANTUM) DYNAMICS: TIME FOR NEW ALGORITHMS



CPU performance (C) K. Rupp

GPU cluster Harvard

`https://www.karlrupp.net/2015/06/40-years-of-microprocessor-trend-data/`

- GPU useful for many different physics applications: electron transport[1], few & many body physics[2], astrophysics[3]
- modern computer require parallel algorithms, excellently suited for (semi)classics!

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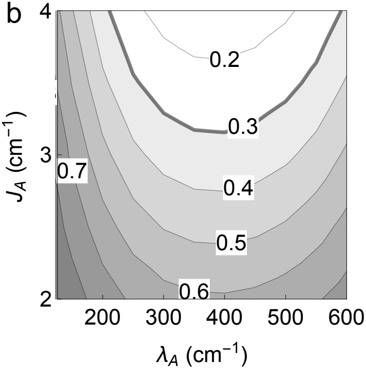
[1] TK: *Time dependent approach to transport and scattering*, AIP Conf Proc 2011

[2] TK et al: *Self-consistent calculation of electric potentials in Hall devices*, Phys Rev B 2010

[3] TK & Noack: *Coma structures observed by Rosetta of comet 67P/Churyumov-Gerasimenko*, APJ Lett 2016

Methods for open quantum system dynamics



Transfered population after 50 ps in *C. tepidum* for different coupling strength $\boldsymbol{\lambda}$ of the antenna [a]

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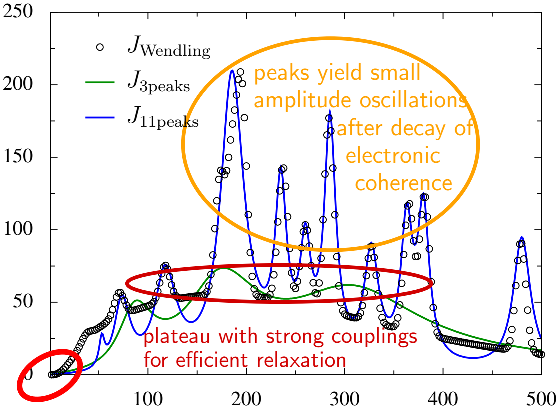
[a] TK, Rodriguez, Sci Rep 2017

Capture strong coupling and non-Markovian effects with exact dynamics:

- stochastic methods (Strunz, Eisfeld)
- t-DMRG (Plenio, Huelga)
- Monte Carlo, QUAPI (Makri)
- HEOM: works best for photosynth (finite $\boldsymbol{T}$), parallel implementations: QMaster, GPU-HEOM (available on `nanohub.org/tools/gpuheompop`)
- semiclassics? (Miller)

Design principles: lessons from bio systems?

- transport determined by properties of vibrational modes
- coherence supports fast initial spreading, later relaxation



peaks yield small amplitude oscillations after decay of electronic coherence

plateau with strong couplings for efficient relaxation

vanishing slope at $\omega \to 0$ suppresses dephasing

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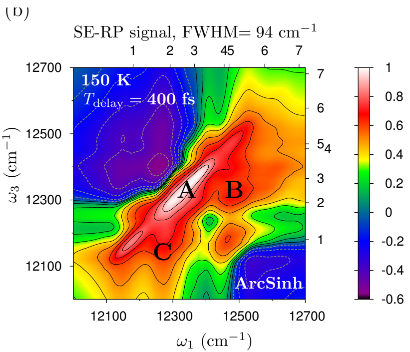
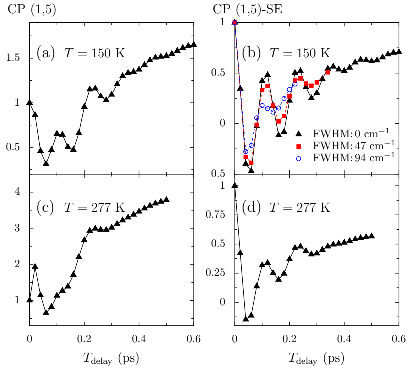
[1] TK, Kreisbeck *Modelling excitonic-energy transfer in LHC* AIP Conf Proc, **1575** 111 (2014)

SIDE-EFFECT: ELECTRONIC COHERENCES AT 277 K





rotational averaging, static disorder
fwhm= **94** cm^{-1}

cross-peak oscillations show electronic coherence at **$T = 277$** K

- both panels: spectral density J(3 peaks)
- electronic coherences are reflected in cross-peaks and possible at **$T = 277$** K

KREISBECK, TK J Phys Chem Lett, **3**, 2828 (2012)

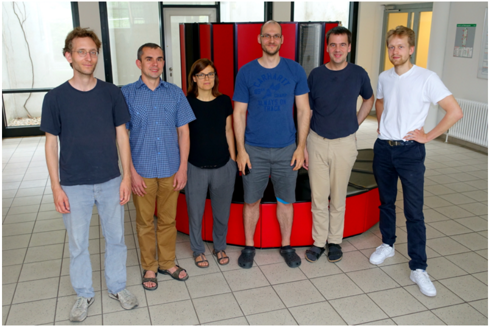
SUMMARY

HEOM transparent inclusion of reorganization effects and coherences

- computational efficient at finite temperature
- direct comparison with experiments

Funding:

- DFG & Heisenberg programme
- EU H2020 Marie-Curie fellowship
- Zuse Institut Berlin (ZIB)



hpc-HEOM team @ZIB in front of Cray-Y-MP/4 supercomputer (3 GFLOP/s), Pascal GPU 4000 GFLOP/s