Photosynthetic light harvesting – control through disorder

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Experimental evidence of coherence in photosynthesis

Zoom into a cryptophyte alga – *Proteomonas sulcata*



[Scholes et al., 2012]

Quantum coherence in "plants" – a provocation!

FMO photosynthetic complex (green sulfur bacteria)

2D spectroscopy



light harvesting antenna complexes (e.g., "FMO") funnel excitations from receptor to reaction center with ≥ 95 % quantum efficiency

at ambient temperature [Engel et al., 2007; Collini et al., 2009; D.B. Turner et al., 2011]

in noisy, multi-hierarchical environment ??? ORIGIN OF THIS EFFICIENCY ???

Difficult experiments on dirty systems!



[Engel et al, 2010 (left), vs. Fleming et al., 2007 (right); NOW WITH ERROR BARS: Turner et al., 2011;

SINGLE MOLECULE experiments: Krüger et al., 2011; Hildner et al., 2012]

Photosynthetic complex of purple bacteria



Scheuring et al., EMBO J. 23 (2004) 4127



Hu et al., Quart. Rev. Biophys. 35 (2002) 1

[talk by Richard Hildner, Freiburg, 2012]

Observations/issues

- extended states; coherence over large distances; ~ 10 Å...100 nm...
- long-lived coherences, in some cases even at ambient temperatures
- . . . longer than typical population transfer times $\sim 200 \dots 300 \text{ fs}$
- widely variable architectures; often disordered systems
- inhomogeneous broadening/dephasing vs. decoherence
- the matrix matters
- need both, effective theoretical descriptions to fit experimental results
- and models with the perspective for conceptual understanding

Complex/"disordered" quantum transport

Exemplary transport problems – nuclear matter



[N. Bohr, 1936]

compound nuclear reactions complex, microscopically uncontrolled dynamics of interacting particles

Exemplary transport problems – condensed matter



[Anderson 1958; Labeyrie et al., 1999]

multiple scattering in a disordered medium coherent superposition of many transmission amplitudes

Exemplary transport problems – atomic matter

near integrable

chaotic



atomic hydrogen in a static magnetic field strong, nonlinear coupling of few degrees of freedom

Exemplary transport problems – soft matter



[T Brixner et al, 2006]

excitation transport in FMO has disorder and strongly coupled (background) degrees of freedom

Disorder/chaos as a handle for coherent control



PRL 96, 063904 (2006) PHYSICAL REVIEW LETTERS week ending 17 FEBRUARY 2006

 Observation of the Critical Regime Near Anderson Localization of Light

 Martin Störzer, Peter Gross, Christof M. Aegerter, and Georg Maret

 PRL 102, 183001 (2009)
 PHYSICAL
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Microwave-Driven Atoms: From Anderson Localization to Einstein's Photoeffect

Alexej Schelle,1,2 Dominique Delande,2 and Andreas Buchleitner1

Quantum-Coherent Electronic Energy Transfer: Did Nature Think of It First?

Gregory D. Scholes*

Department of Chemistry, Institute for Optical Sciences and Centre for Quantum Information and Quantum Control, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6 Canada

Direct observation of Anderson localization of matter waves in a controlled disorder

Juliette Billy¹, Vincent Josse¹, Zhanchun Zuo¹, Alain Bernard¹, Ben Hambrecht¹, Pierre Lugan¹, David Clément¹, Laurent Sanchez-Palencia¹, Philippe Bouyer¹ & Alain Aspect¹

Transport and Anderson localization in disordered two-dimensional photonic lattices

Tal Schwartz¹, Guy Bartal¹, Shmuel Fishman¹ & Mordechai Segev¹



Hence, a statistical, coherent transport model rather than an effective, open system dynamical description!

Stark physical abstraction

FMO as a 3D random network of sites –
 coherent dynamics on finite, fully connected, random graph –



•
$$H = \sum_{i \neq j=1}^{N} v_{i,j} \sigma_{+}^{(j)} \sigma_{-}^{(i)}$$

- intersite coupling $v_{i,j} \sim r_{i,j}^{-3}$
- excitation injected at "in"
- excitation delivered at "out"
- remaining sites randomly placed within sphere
- efficient \equiv large p_{out} , after short times

Transport efficiency

time evolution of on-site probabilities $p_i = |\langle i | U(t) | in \rangle|^2$



Transport efficiency vs. configuration



 \rightarrow rare, optimal configurations – mostly "localized" transport \leftarrow

Typical evolution and configuration



OPTIMIZE!

Optimal evolution and configuration

optimized population dynamics

optimized configuration

out



excitation perfectly refocusses on output! optimization by genetic algorithm from typical configuration evolution might have done the same!?!

Design principles

Model ingredients



an incident of optimal dynamics

- centro-symmetric Hamiltonian H, HJ = HJ, $J_{i,j} = \delta_{i,N-j+1}$
- *H* has "dominant doublet", i.e. eigenvectors $|\tilde{\pm}\rangle$ with

 $|\langle \tilde{\pm}, \pm \rangle|^2 > \alpha \approx 1 \,,$

where

 $|\pm\rangle = (|\mathrm{in}\rangle \pm |\mathrm{out}\rangle)/\sqrt{2}$

• *H* randomly sampled from Gaussian Orthogonal Ensemble (GOE)

Distribution of efficiencies for distinct design principles



dramatic efficiency enhancement . . .

... if centrosymmetric with dominant doublet!! [Walschaers et al., 2013]

Statistically robust distribution of inverse transfer times

Size, density of states, average coupling strength doorway sites-bulk ALONE matter!



optimal configurations in algebraic tail!

In biological functionality coherence *could* matter, since . . .

- . . . constructive multipath interference enhances efficiency
- . . . optimal conformations are not too rare
- . . . conformational details don't matter for statistics
- statistical control of function by disorder and redundancy !?!
- generic picture of quantum system with not too many, strongly coupled (here: *vibrational and electronic*) degrees of freedom (CAT)

[Tomsovic & Ullmo, 1994; Zakrzewski et al., 1998]

What's missing for a deeper understanding

- predictive/<u>falsifiable</u> theory on experimentally accessible observables
- experimental means for targeted intervention
- role of superstructure(s) in space and time
- scenarios for functional relevance of microscopic coherence

Literature/Propaganda



Semiconductors and Semimetals
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Sci. 5, 9374 (2012); PRL 111,
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2011; diploma Tobias Zech, 2012;
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