Quantum effects in complex materials: Determinism, statistics, structure

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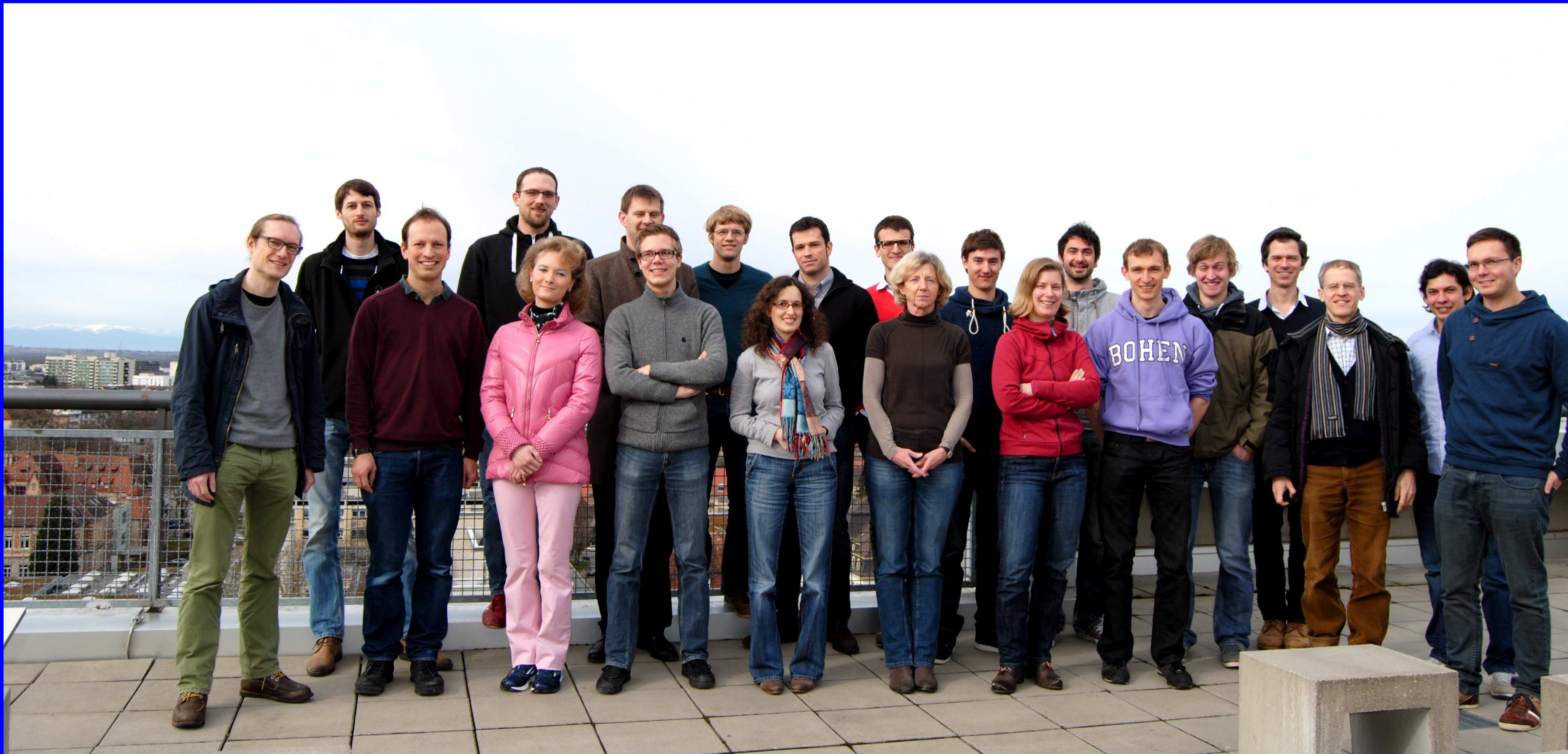
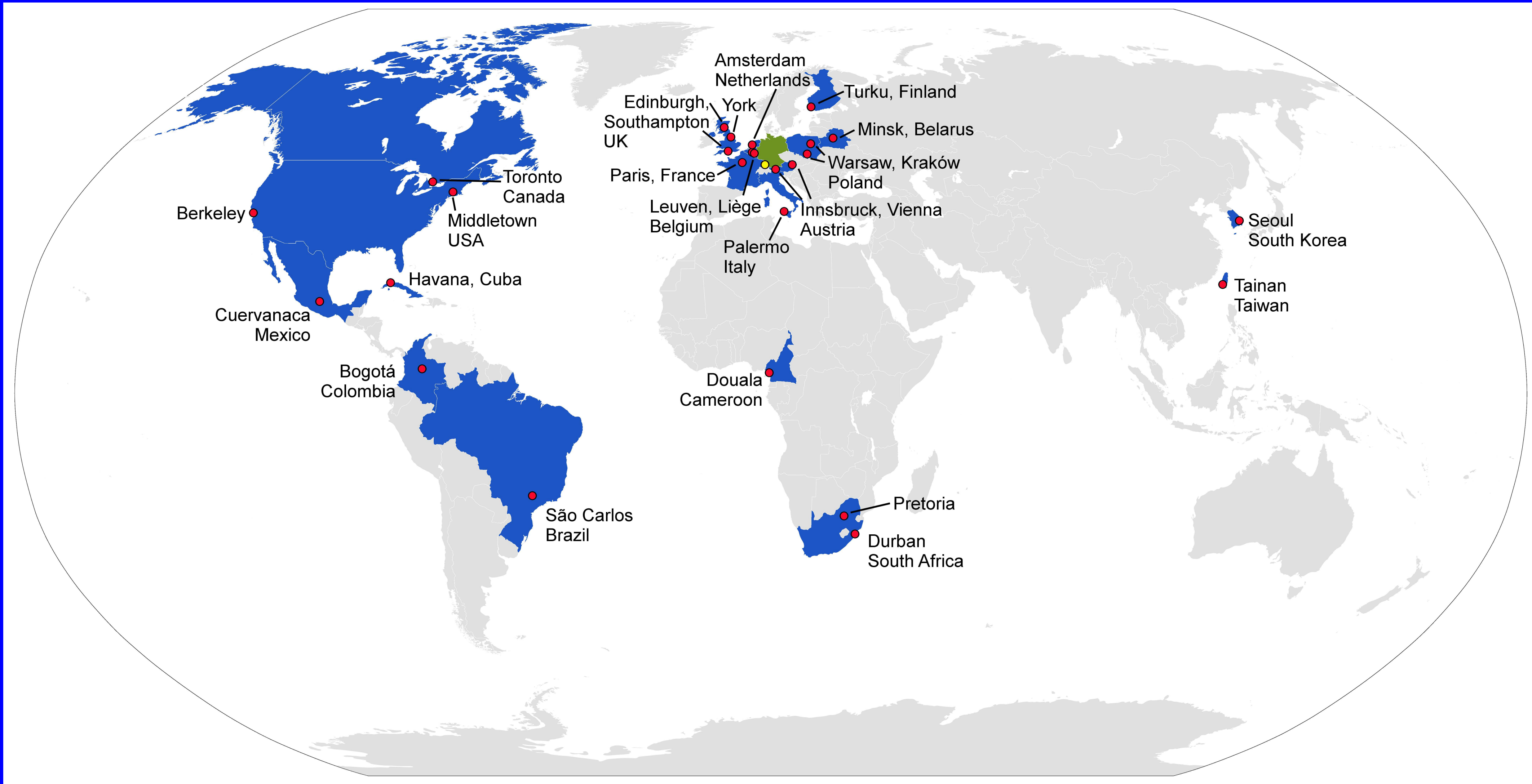
Nonlinear Dynamics in Quantum Systems

Fundamental Problems in Quantum Physics, Erice, 25 March 2015

Nonlinear Dynamics in Quantum Systems



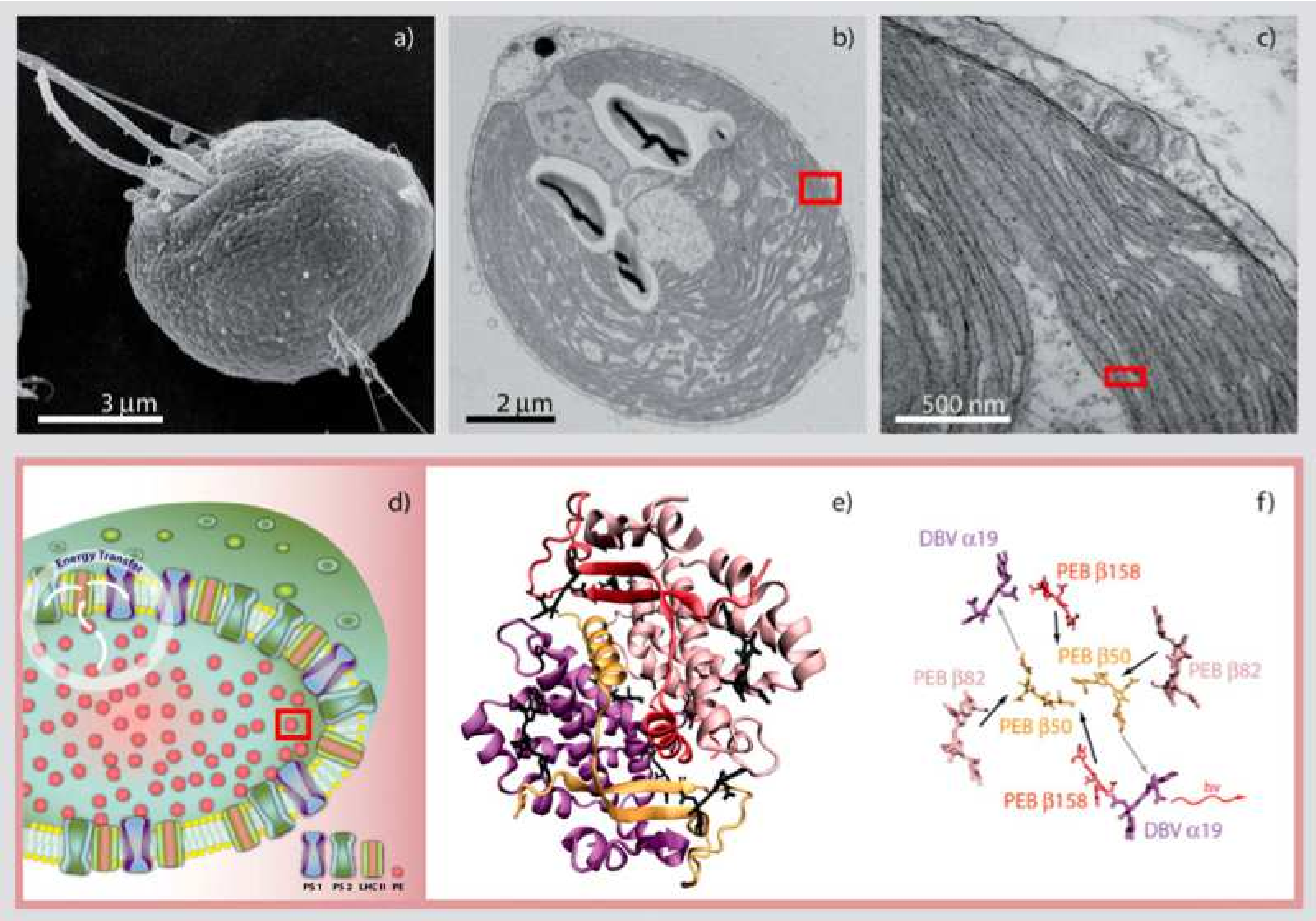
In Collaboration with . . .



funded by DFG, DAAD, AvH and VolkswagenStiftung

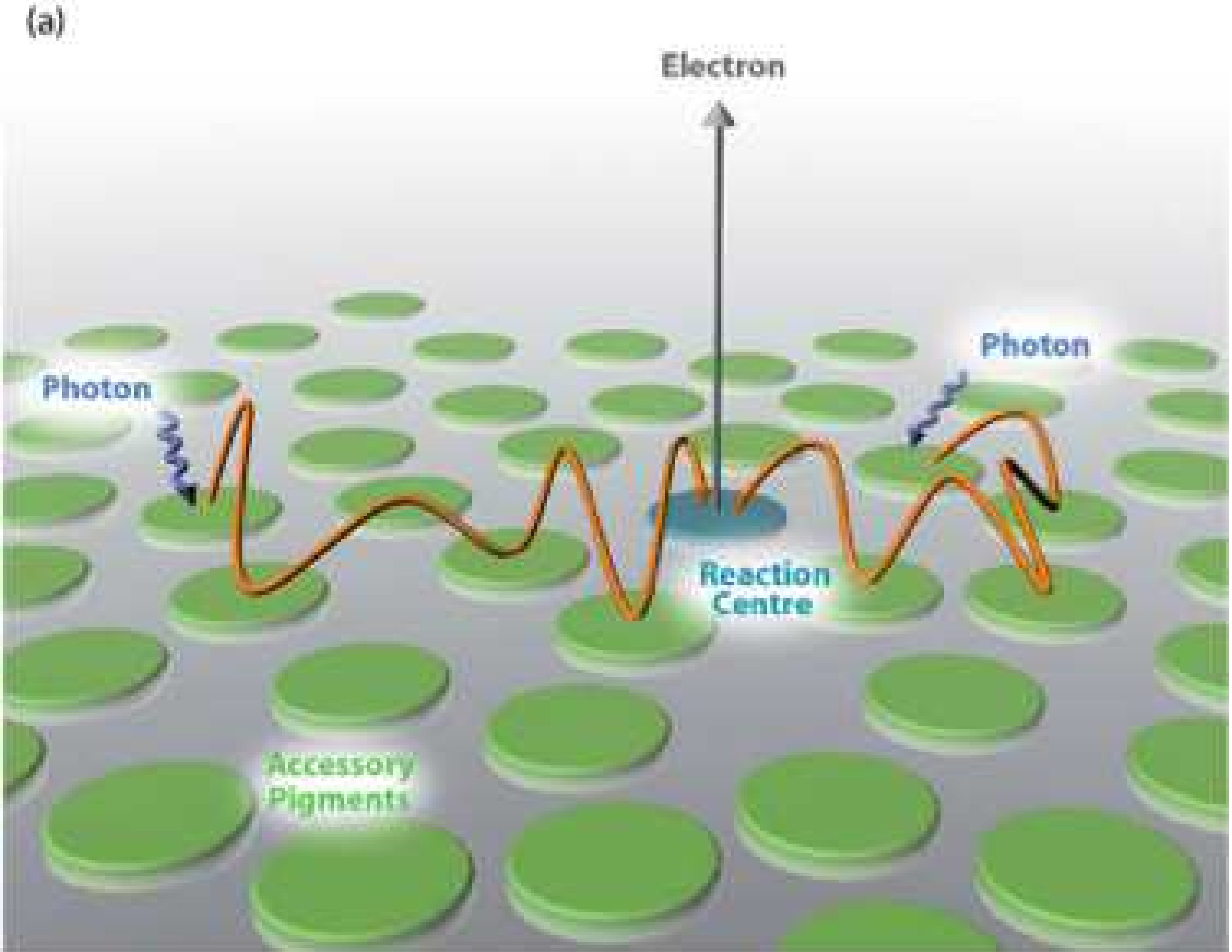
Complex materials

Cryptophyte alga – *Proteomonas sulcata*



[Scholes et al., 2012]

Light harvesting: a (quantum?) transport problem



Essential ingredients

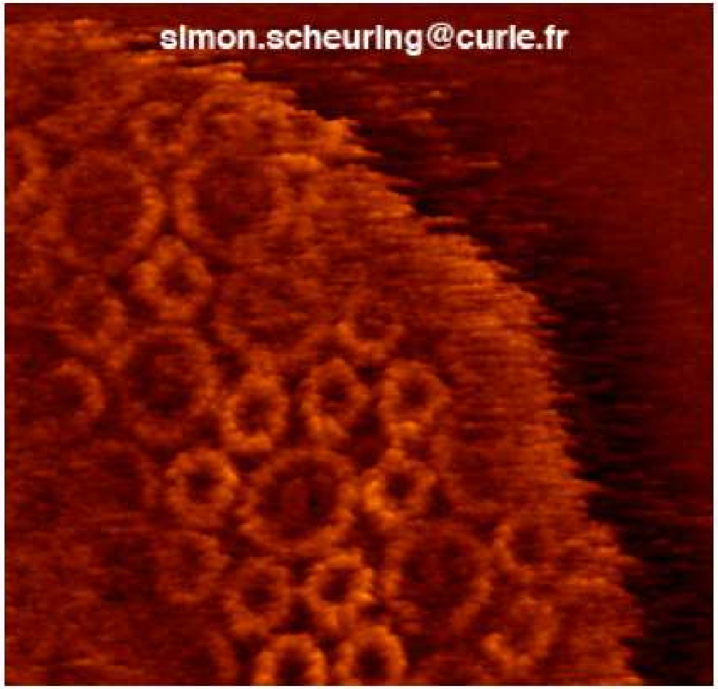
- electronic degrees of freedom
- vibrational (“scaffold”, “background”) degrees of freedom
- disorder (vs. effective Hamiltonians)
- controlled, robust structural features
- noise

$$\sum_{\text{all this}} \ldots = \mathbf{COMPLEXITY}(???!?)$$

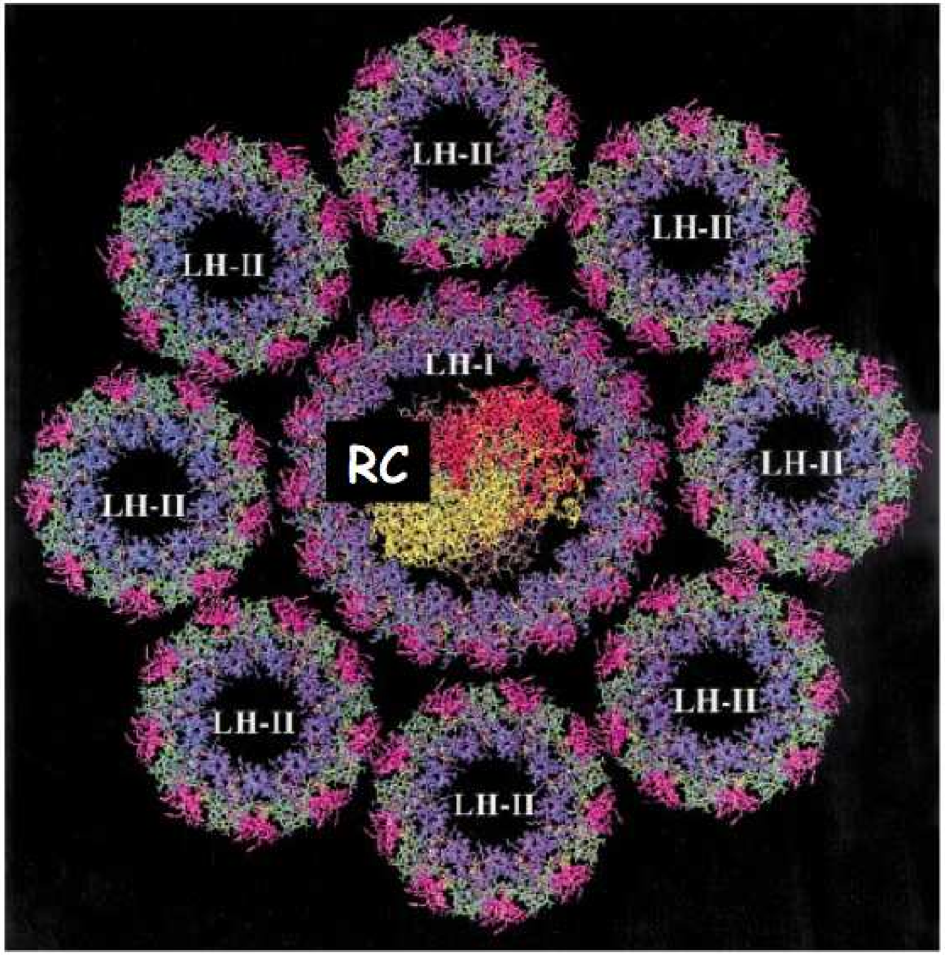
Other incarnations

[see also bird navigation, olfaction – essentially same story line]

Photosynthetic complex of purple bacteria



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



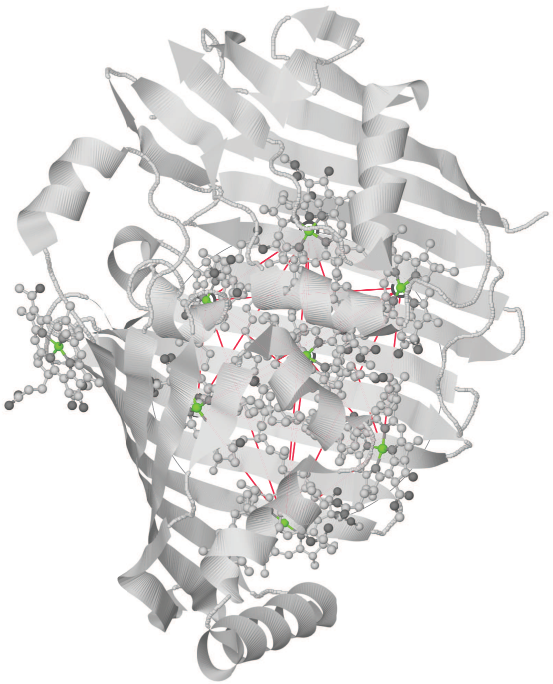
Hu *et al.*, Quart. Rev. Biophys. **35** (2002) 1

[talk by Richard Hildner, Freiburg, 2012]

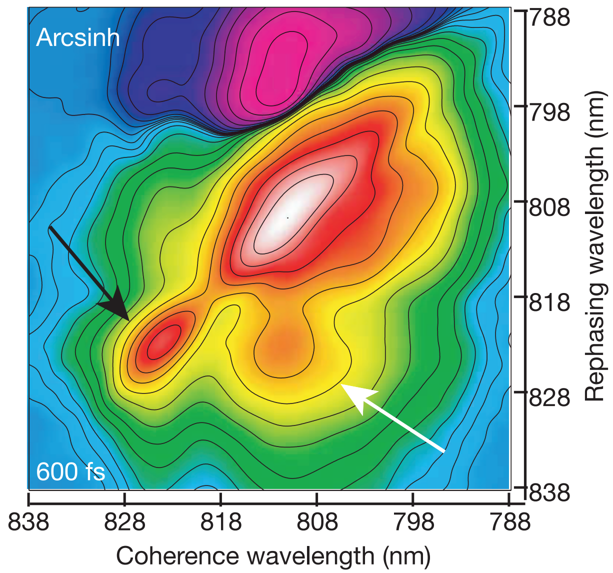
Experimental phenomenology

Quantum coherence in "plants" – a provocation!

FMO photosynthetic complex (green sulfur bacteria)



2D spectroscopy



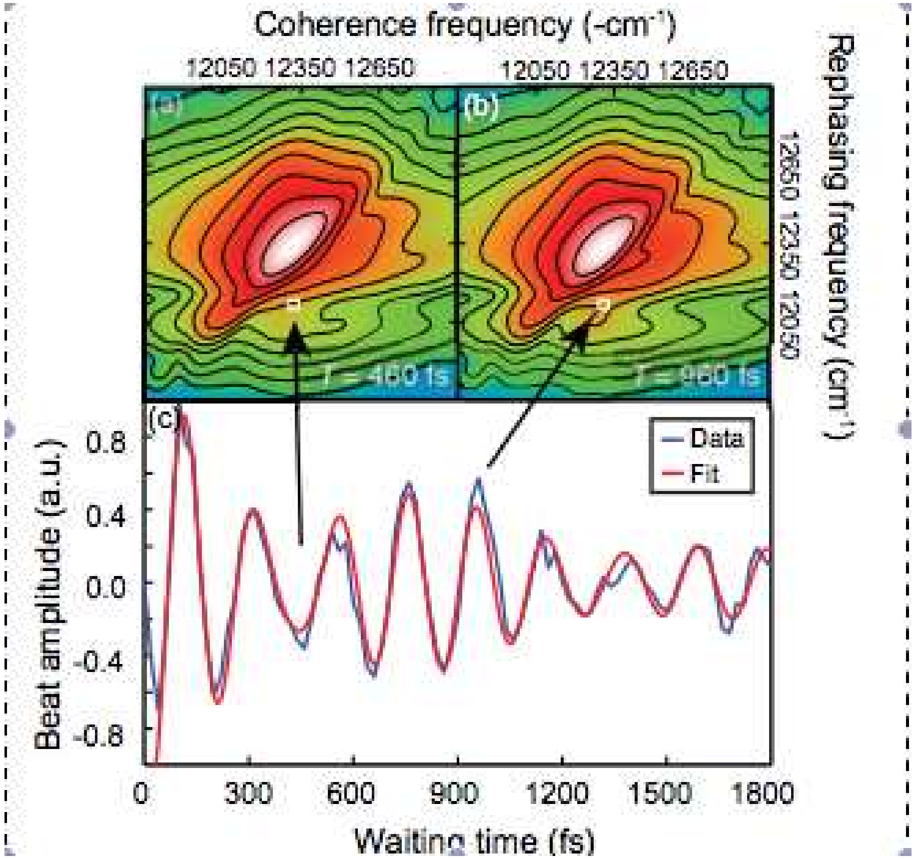
light harvesting antenna complexes (e.g., "FMO") funnel excitations from receptor to reaction center with $\geq 95\ \%$ **quantum efficiency**

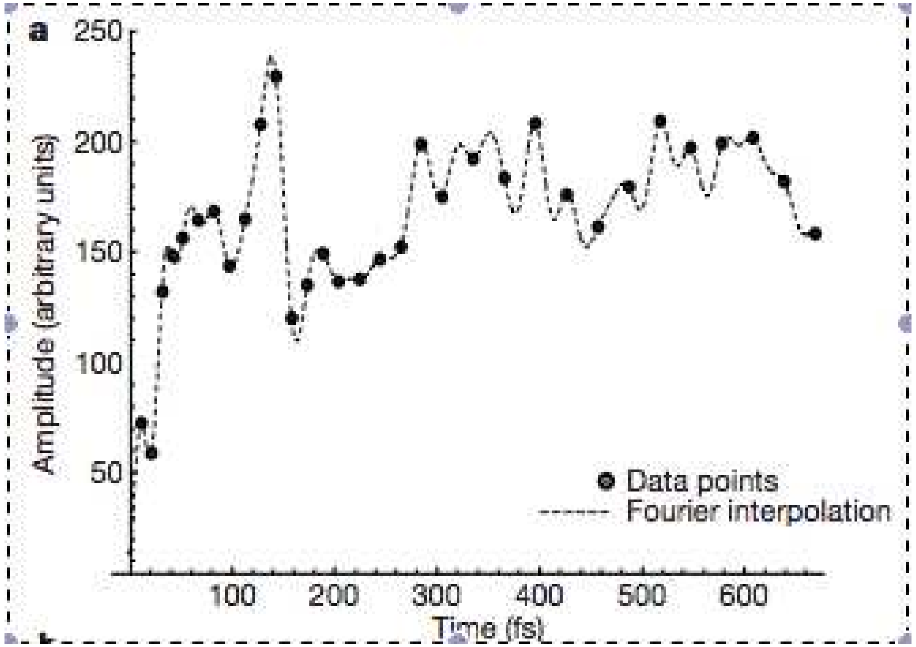
at ambient temperature [Engel et al., 2007; Collini et al., 2009; D.B. Turner et al., 2011]

in noisy, multi-hierarchical environment

??? ORIGIN OF THIS EFFICIENCY ???

Difficult, beautiful 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;

ALSO see charge separation in PHOTOVOLTAIC BLENDS: Falke et al, 2014]

Conjugated polymer chains

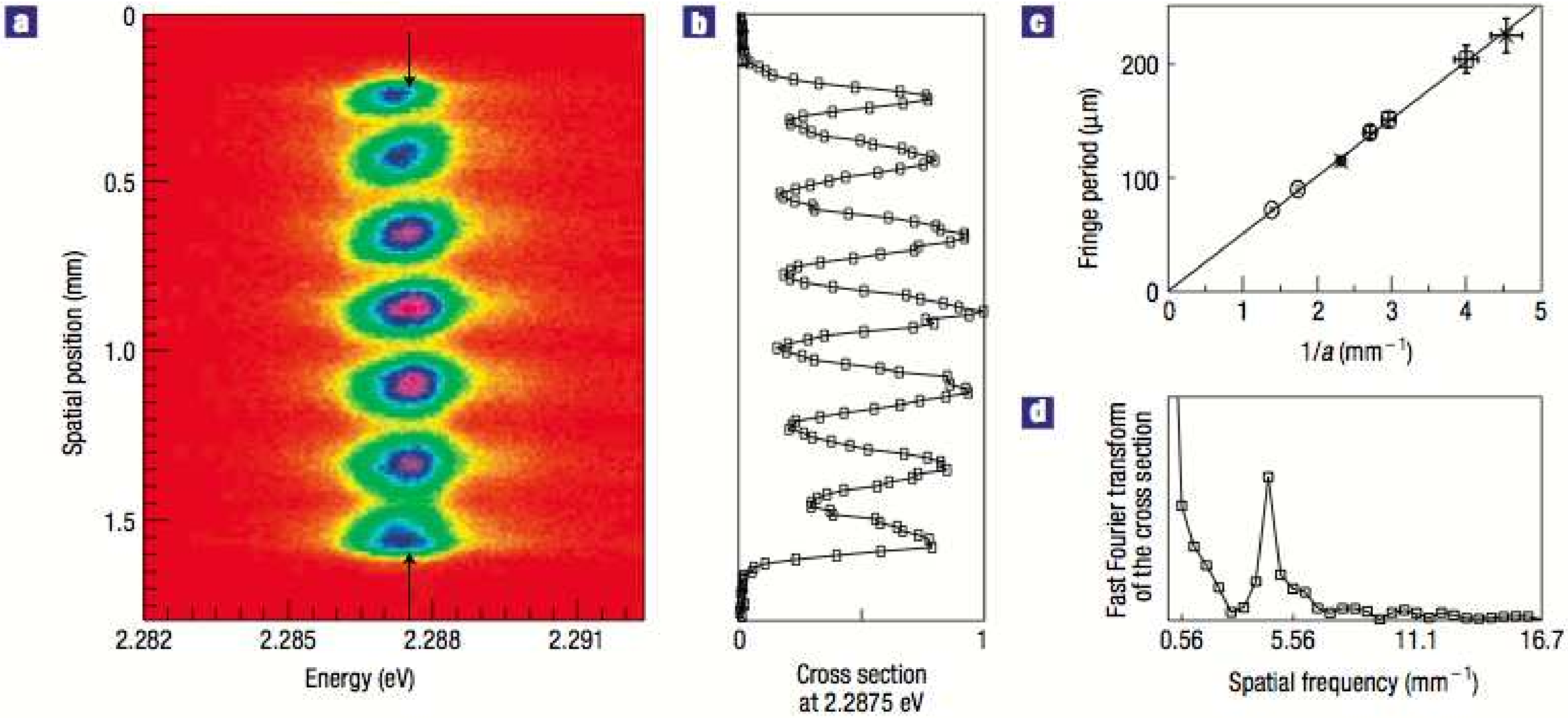


Figure 2 Interference pattern of a single-chain emission. a, Interference pattern obtained from two 1-µm-wide emitting regions of a 10-µm-long chain. This interference pattern is observed in the Fourier plane formed in the focal plane of the spectrometer entrance lens. The pattern length is limited by the collecting optics. The separation between the two sources taken out of the chain is about 2 µm. The corresponding distance in the plane of the slits is around 220 µm leading to the fringe period of about 225 µm. **b**, Cross-section of the previous interference pattern at 2.2875 eV (see arrows in Fig. 2a) showing the intensity profile which gives a value of the contrast $C=(I_{max}-I_{min})/(I_{max}+I_{min})$ of 75%. I_{min} and I_{max} and the minimum and maximum intensity respectively. **c**, Plot of the fringes period as a function of the distance between the two interfering regions. The plot shows the results obtained for three experiments each performed on an individual chain (squares, circles and crosses). The fringe period scales as $\lambda f/a$ as shown by the straight line. The scaling factor λf only depends on the wavelength λ of the emission and on the focal length f of the spectrometer entrance lens. The error bar on the value of the fringes period is related to the Fourier transform analysis, which gives the value of the spatial frequency. The uncertainty is given by the separation between two points in the Fourier transform. It leads to a varying uncertainty on the fringe period. The error bar on $1/a$ corresponds to a constant 5-µm reading uncertainty on a. **d**, Fourier transform of the cross-section presented in **b**. A single spatial frequency appears corresponding to the fringe period.

[Dubin et al (2005)]

Observations

- **coherence** over large distances; $\sim 10\ \text{Å} \ldots 100\ \text{nm} \ldots$

- "long-lived", *transient* coherences (e.g., at ambient temperatures) $\sim 200 \ldots 300\ \text{fs}$

- widely variable architectures; essentially always garnished with "**disorder**", along with some **robust/coarse grained structural** features and **redundancy**

- disorder is *distinct* from **noise**; strongly affects transport

- the **matrix** matters

$\rightarrow$ need both, *effective theoretical descriptions to fit experimental results*, and
<u>*models with the perspective for conceptual understanding*</u>

Determinism, statistics, structure

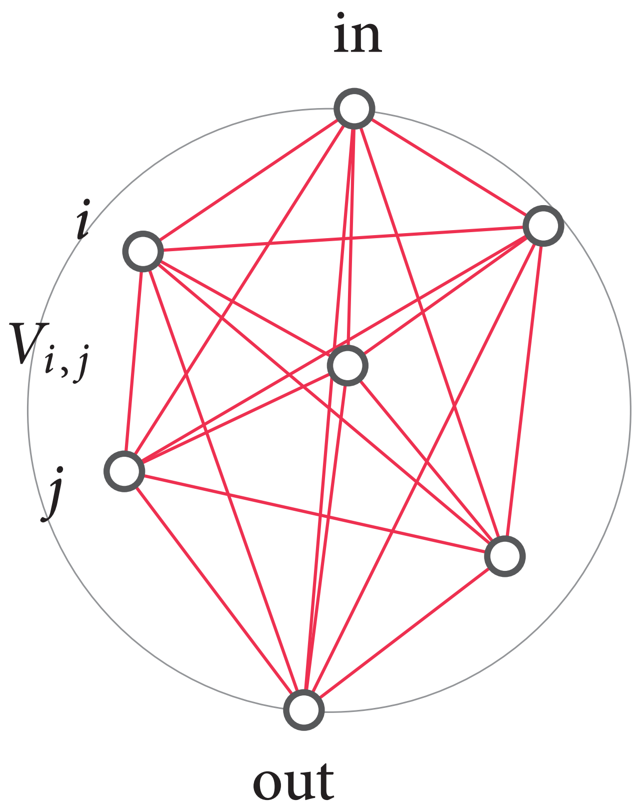
minimal model, to account for

vibr-onic coupling, disorder, structure (no noise – too slow)

[*implicit* in advanced quantum dynamical treatments]

Simplified, deterministic model – e.g., of FMO

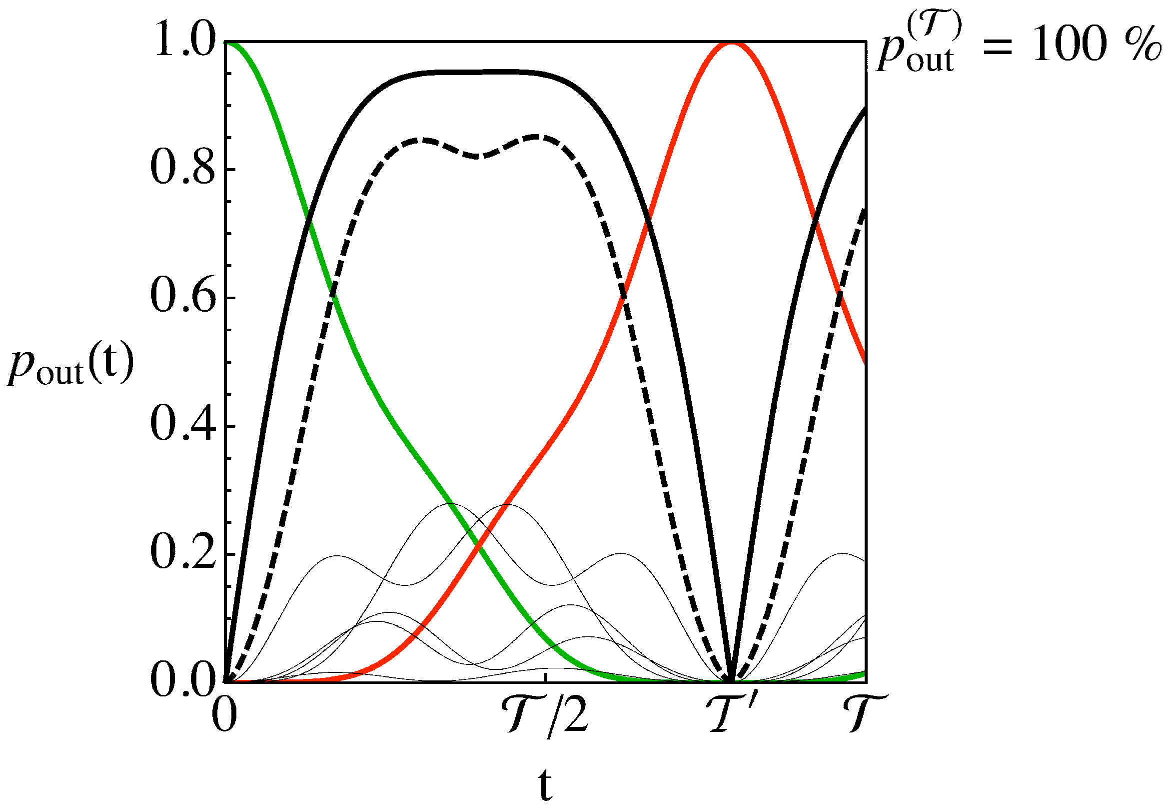
– FMO as a 3D random network of sites –



- $H = \sum_{i \neq j=1}^{N} v_{i,j} \sigma_+^{(j)} \sigma_-^{(i)}$
- intersite coupling $v_{i,j} \sim r_{i,j}^{-3}$
- excitation injected at “in”
- excitation delivered at “out”
- remaining sites randomly placed within sphere
- efficiency $\equiv$ large p_{out}, after short times

Model ingredients for constrained randomness

an incident of optimal dynamics



[Scholak et al., 2011]

- **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

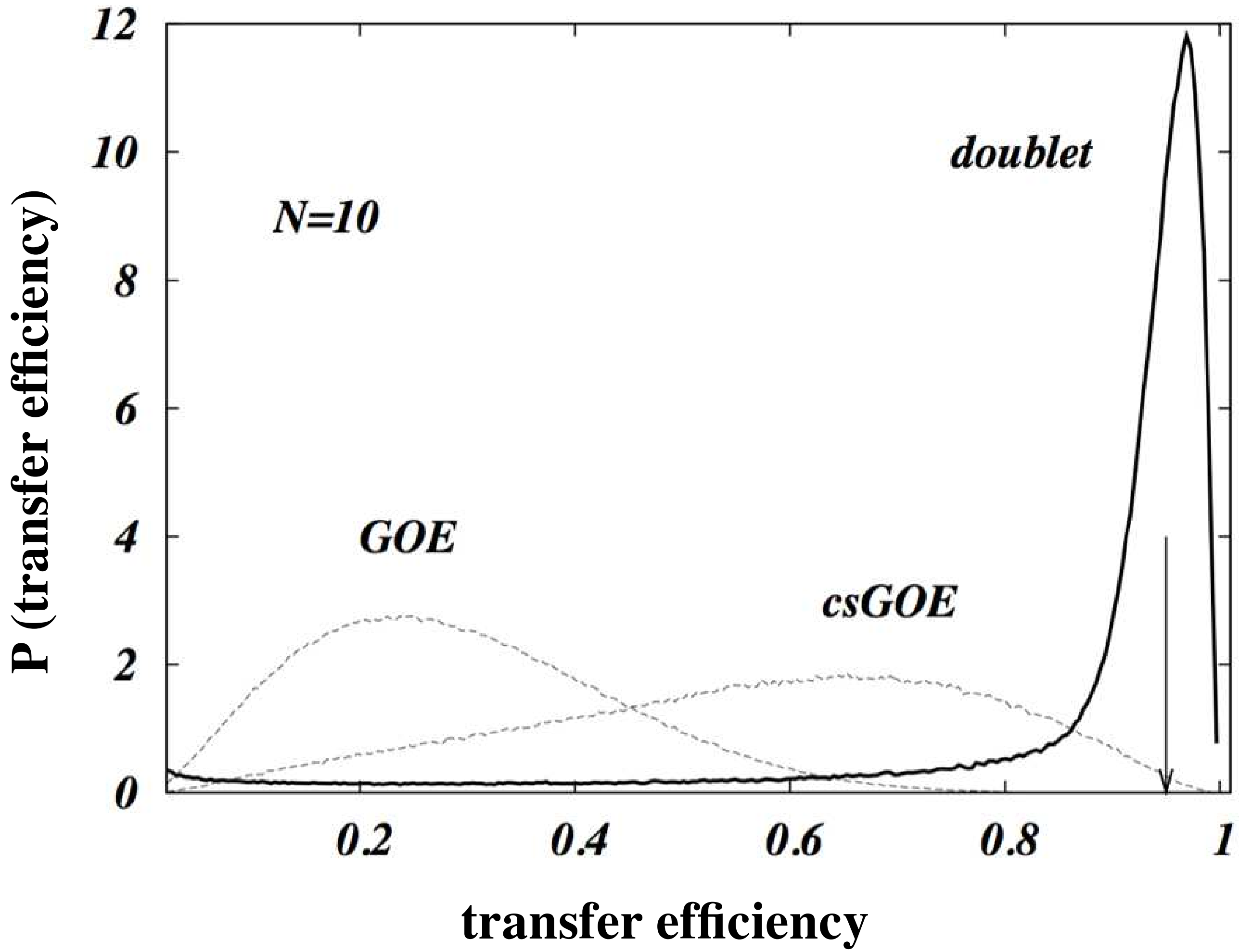
$$|\pm\rangle = (|\text{in}\rangle \pm |\text{out}\rangle)/\sqrt{2}$$

- H **randomly sampled**

- **chaos assisted tunneling in double well coupled to second dof**

Control the *distribution* of transfer efficiencies

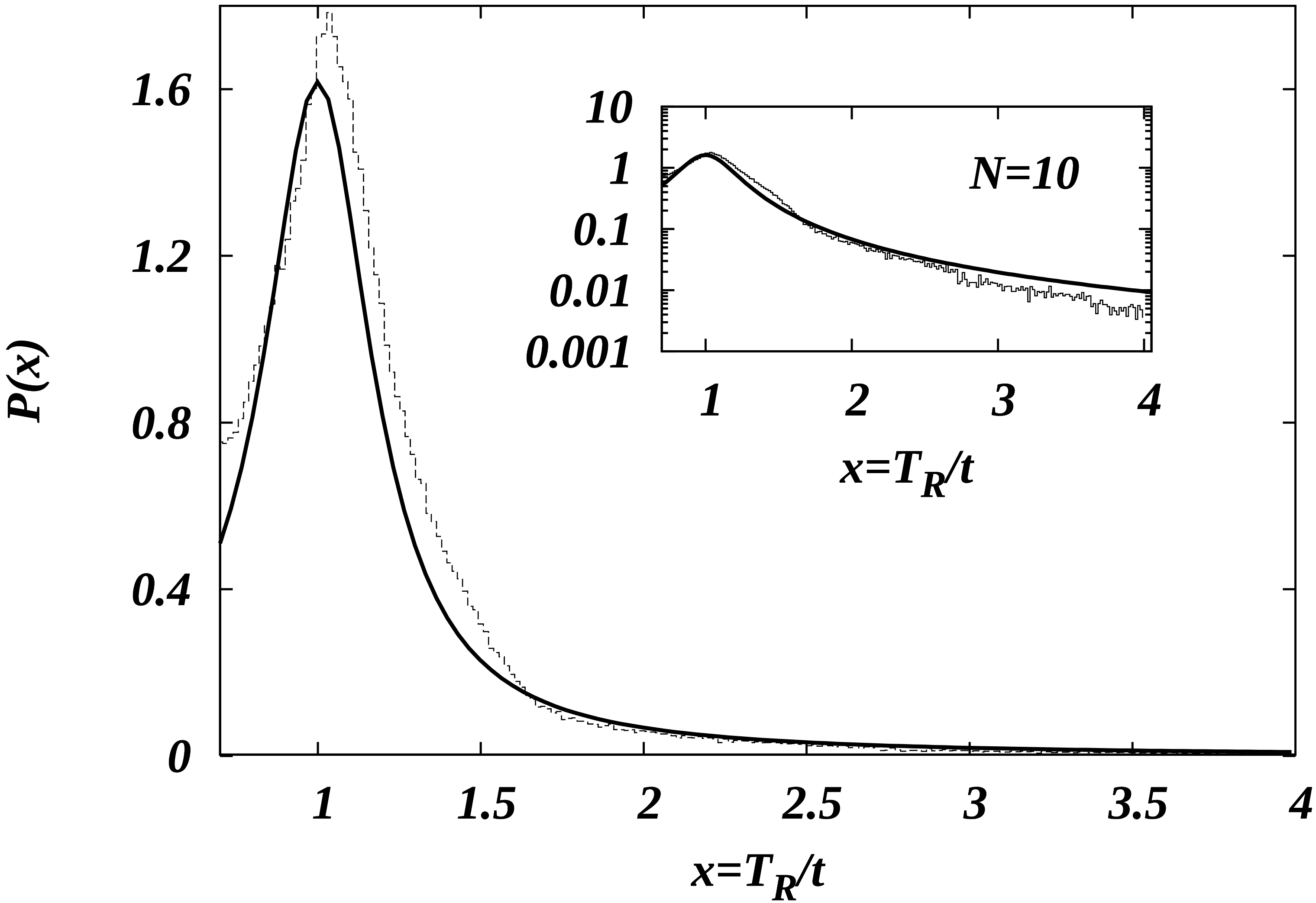
dramatic efficiency enhancement . . .



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

Statistically robust distribution of inverse transfer times

fastest configurations in *algebraic* tail!



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

What have we done?

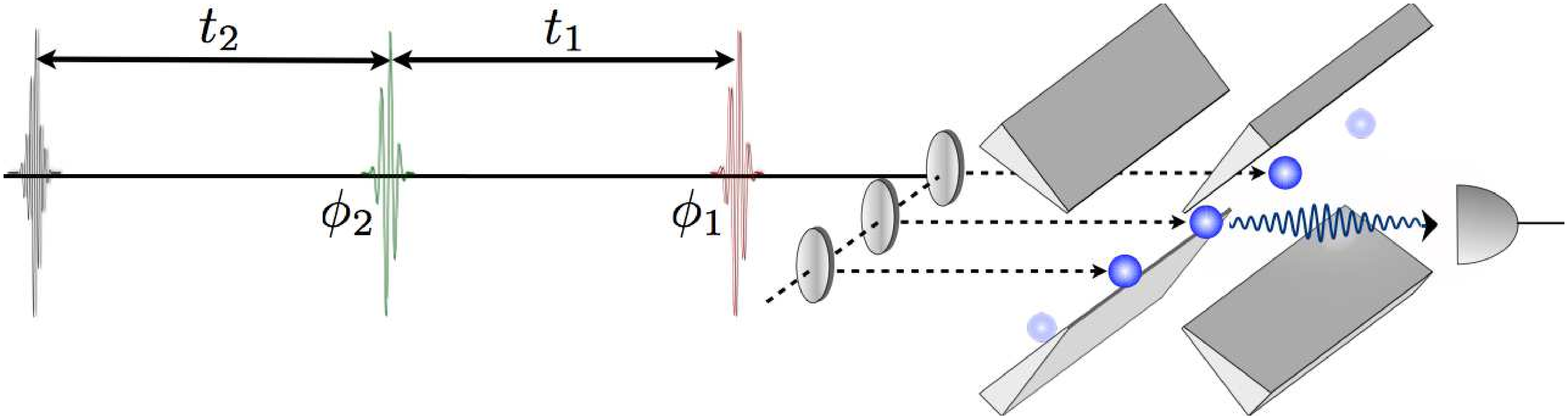
- established elements of a minimal statistical model with
  - coherent, deterministic, rapid transport . . .
  - . . . mediated by collective coupling to intermediate sites
  - coarse grained structural elements
  - disorder
- which guarantees robust, efficient transport (even in presence of noise)

consistent with other observations, also in experiments, but not yet predictive!

[e.g., Kolli et al., 2012; Mancal et al., 2012; Ramanan et al., 2015]

What’s missing for a better understanding

Even cleaner experiments

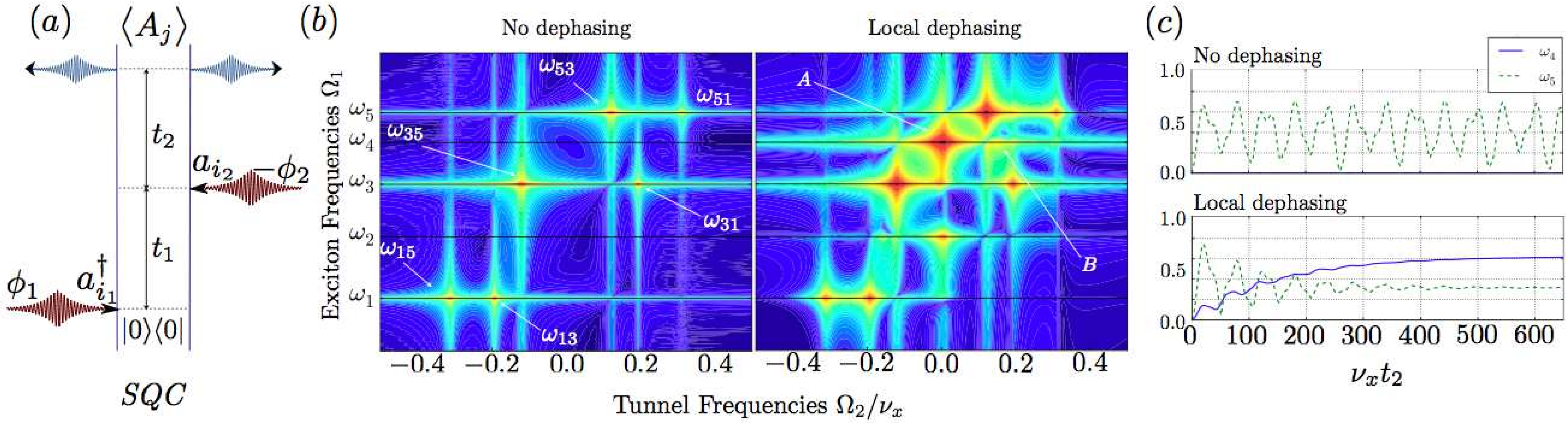


[Schlawin et al., 2014; Gessner et al., 2014; Lemmer et al, 2015]

2D spectroscopy with single-site addressability – as in ion traps

well-defined initial conditions, read-out, coupling-in/-out, statistics

E.g., coherent vs. incoherent transport



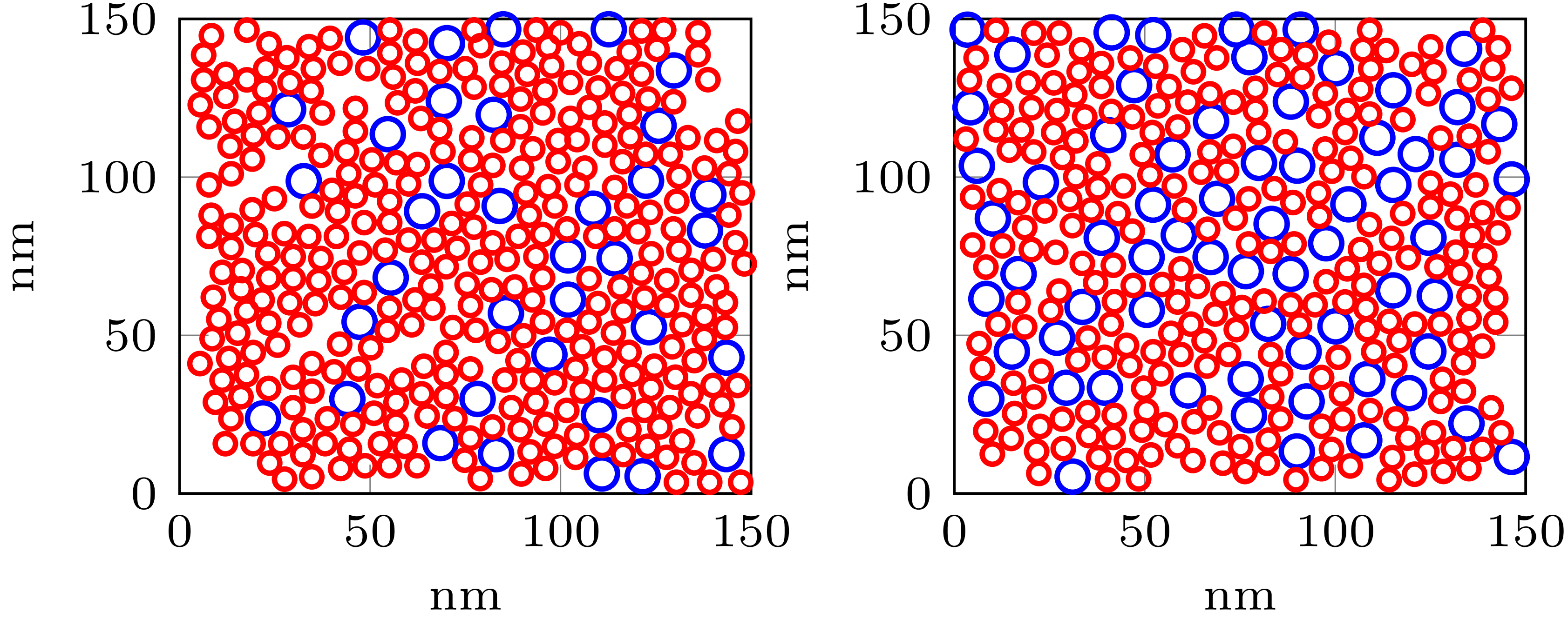
[Schlawin et al., 2014; Gessner et al., 2014]

dephasing-induced population of otherwise “dark” ω_4-state

unambiguous signature in zero-frequency 2D signal

Clarify rôle and hierarchy of superstructures

LHI (blue)-LHII (red) distribution in photosynthetic membrane of Rhodopseudomonas sphaeroides



[Scheuring & Sturgis, 2005]

Membrane structure under low- (left) and high-light (right) conditions

How (if at all) are quantum and classical processes matched for functionality?

Angelo's guiding questions

What is it about?

– mimic nature e.g. for sustainable light-energy conversion

What is true about it?

– transient vibronic coherences in many complex materials

What is false about it?

– noise assisted transport as a quantum enhanced process; purely electronic coherences

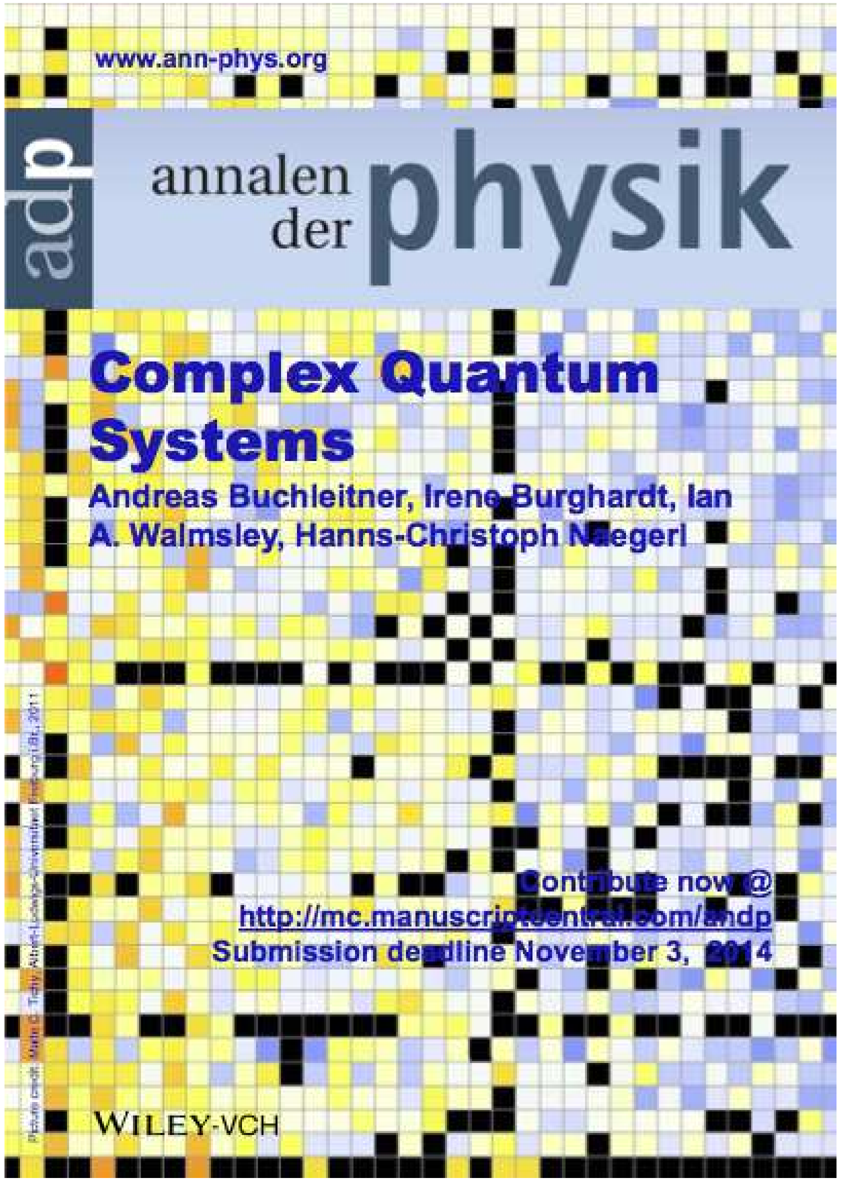
What has been achieved?

– experiments; by now more humble/sober theory approaches

Open problems?

– sun vs. laser; switch off coherence; diversified scenarios; functional relevance

Literature/Propaganda



– Semiconductors and Semimetals 83, 1 (2010); PRE 83, 021912 (2011); EPL 96, 10001 (2011); JPB 44, 184012 (2011); Energy Environ. Sci. 5, 9374 (2012); PRL 111, 180601 (2013); PRA 90, 023603 (2014); NJP 16, 055002, 092001 (2014); – PhD Torsten Scholak, Freiburg 2011; diploma Tobias Zech, 2012; PhD Simeon Sauer, 2013; PhD Jochen Zimmermann, 2015; PhD Frank Schlawin, 2015; PhD Manuel Gessner, 2015; PhD Mattia Walschaers, 2015

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