Quantumness from ultrafast spectroscopy

Animesh Datta
Max Marcus, George Knee, Luke Smith

Department of Physics, University of Warwick, UK

February 1, 2018

International Symposium on New Frontiers in Quantum Correlations
(ISNFQC18), Calcutta, India

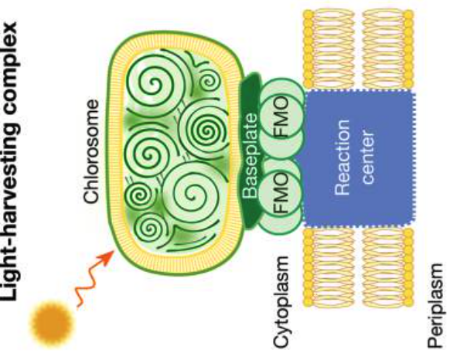
EPSRC Engineering and Physical Sciences Research Council
UK NATIONAL QUANTUM TECHNOLOGIES PROGRAMME
[dstl]
Royal Commission for the Exhibition of 1851

Excitonic energy transport (EET)

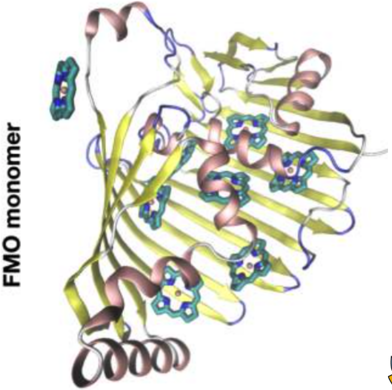
Quantum machine for efficient light harvesting

- Efficient?
- Quantum?

- Studied for decades
- During the last decade using ultrafast optical spectroscopy



Valleau *et al.*, ACS Cent. Sci. **3**, 1086, (2017)



The hype

HORIZON
The EU Research & Innovation Magazine

HOME | KEY THEMES | VIEWS | TOPICS | MEDIA

Rece

ENVIRONMENT ENERGY

Vibrating molecules help plants make use of quantum effects

11 May 2015

by Joanna Roberts

Understanding how plants use quantum mechanics in photosynthesis could contribute to the design of mo efficient solar cells. Image: Shutterstock/ArTDi101

The mysterious properties of quantum mechanics are helping scientists understand how plants can photosynthesise energy so efficiently, and the fin could help design more efficient solar cells.

It's part of the emerging research field of quantum biology, which is looking at the role quantum mechanics plays in biological systems.

Until recently, it was thought that quantum effects could only be observed in a system where there was minimal interference from the environment, for example a system th was cooled to near absolute zero to reduce the thermal vibrations of molecules. Biolog systems were considered too complex for quantum descriptions to apply.

arXiv.org > physics > arXiv:1610.08425

Physics > Biological Physics

Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer

Hong-Guang Duan, Valentyn I. Prokhorenko, Richard Cogdell, Khuram Ashraf, Amy L. Stevens, Michael Thorwart, R. J. Dwayne Miller

(Submitted on 26 Oct 2016)

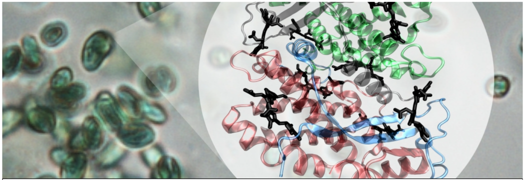
During the first steps of photosynthesis, the energy of impinging solar photons is transformed into electronic excitation energy of the light-harvesting biomolecular complexes. The subsequent energy transfer to the reaction center is understood in terms of exciton quasiparticles which move on a grid of biomolecular sites on typical time scales less than 100 femtoseconds (fs). Since the early days of quantum mechanics, this energy transfer is described as an incoherent Forster hopping with classical site occupation probabilities, but with quantum mechanically determined rate constants. This orthodox picture has been challenged by ultrafast optical spectroscopy experiments with the Fenna-Matthews-Olson protein in which interference oscillatory signals up to 1.5 picoseconds were reported and interpreted as direct evidence of exceptionally long-lived electronic quantum coherence. Here, we show that the optical 2D photon echo spectra of this complex at ambient temperature in aqueous solution do not provide evidence of any long-lived electronic quantum coherence, but confirm the orthodox view of rapidly decaying electronic quantum coherence on a time scale of 60 fs. Our results give no hint that electronic quantum coherence plays any biofunctional role in real photoactive biomolecular complexes. Since this natural energy transfer complex is rather small and has a structurally well defined protein with the distances between bacteriochlorophylls being comparable to other light-harvesting complexes, we anticipate that this finding is general and directly applies to even larger photoactive biomolecular complexes.

THE ROYAL SOCIETY

Venue hire | Contact us | Fellow login | Search

Home | Fellows | Events | Grants, Schemes & Awards | Topics & policy | Journals | Collections | About us | News

Quantum secrets of photosynthesis



Cryptophyte algae and light-harvesting complex found in this algae. Quantum physics may explain how photosynthesis is so efficient, and teach us a lesson in green energy harvesting. Credit: Alexandra Olaya-Castro, UCL

Hands-on at the exhibit

- Control an animation of the journey of a photon with our interactive plant. Zoom in on diverse light-harvesting molecules.

Summer Science Exhibition 2016

Exhibits

Why do I/we care ?

- Physics: Comparable system & system-bath energy scales
- Chemistry: Excitons dynamics in organic systems

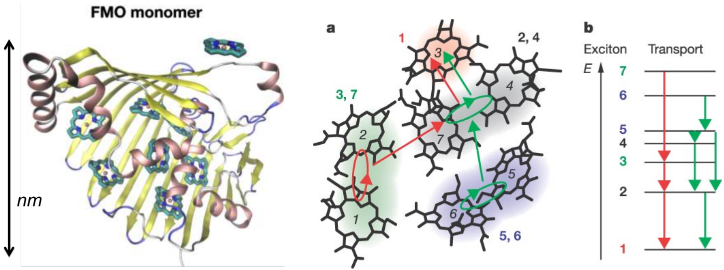


Figure: Femma-Matthews-Olson (FMO) complex

- Engineering: Design principles for artificial light harvesting

?? Biology: Does evolution exploit/use quantum mechanics?

Valleau *et al.*, ACS Cent. Sci. **3**, 1086, (2017)

- Very few naturally occurring light harvesting complexes

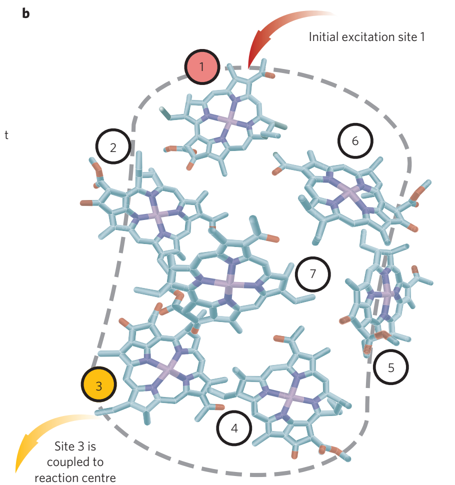
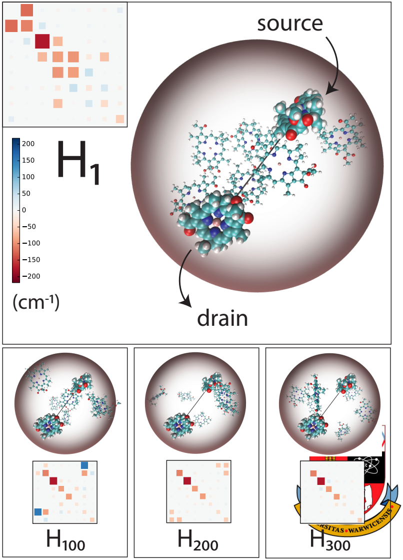


Figure: Fenna-Matthews-Olson monomer



Structure-dynamics relations

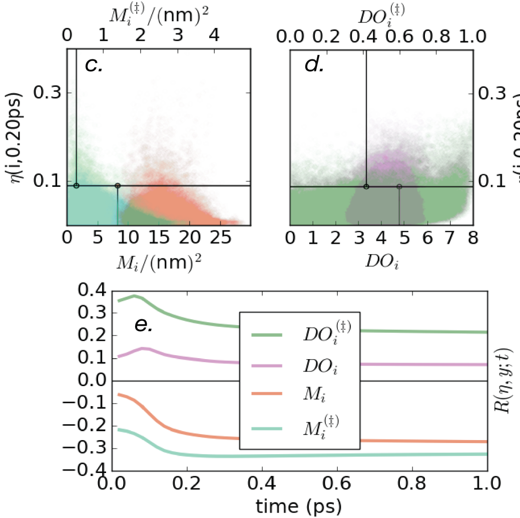
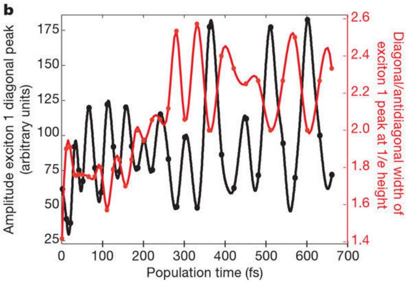


Figure: Correlations about 3.3× with special chromophore

Knee/Rowe/Smith/Troisi/AD, J. Phys. Chem. Lett., **8**, 2328, (2017)

- Quantum coherence in excited state dynamics of FMO



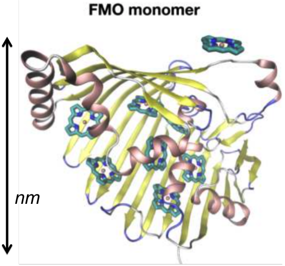


Figure: Ultrafast 4-wave mixing experiment | Engel et al. Nature **446**, 782 (2007) |

- Various calculations of entanglement, nonclassicality
  | Caruso, AD, Wilde, Sarovar, ... | | Li/Lambert/Chen/Chen/Nori, Sci. Rep. **2** (2012) |
- Due to exciton-vibrational coupling | Thyrhaug et al. JPCL **7**, 1653 (2016) |
- Is quantumness present in EET?

What is quantumness?

- Canonically, Bell inequality
- Experimental test against <u>local</u> hidden variable theory
- Space-like separations and swift measurements
- Infeasible to implement on *nm*-scale complexes

What is quantumness?

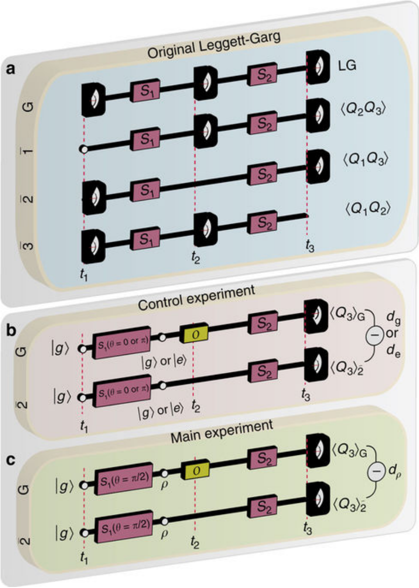
- Canonically, Bell inequality
- Experimental test against local hidden variable theory
- Space-like separations and swift measurements
- Infeasible to implement on *nm*-scale complexes

- Correlations across time rather than space – Leggett Garg
- Test against 'macro realism'
- Requires two-time correlations

Leggett/Garg, PRL **54**, 857 (1985)

Home's talk

No-signalling-in-time



- Simpler and more effective test of macrorealism

  Clemente/Kofler, PRL, **116**, 150401 (2016)

  Knee *et al.* Nat. Comm. **7**,13253 (2016)

- ~~Requires two-time correlations~~
- Needs *fs*-scale time resolution
- ➜ Ultrafast optical spectroscopy

No-signalling-in-time

- A simpler and more effective test of macrorealism
- Mathematically,

$$W_{\Pi_b}(\rho) = \mathrm{Tr}[\Pi_b \cdot \rho] - \mathrm{Tr}[\Pi_b \cdot (\Gamma \circ \rho)], \quad \text{where} \quad I \geq \Pi_b \geq 0$$

  is the difference of probabilities on whether or not the Γ acts
- $\Gamma \circ \rho = \sum_i |i\rangle\langle i|\rho|i\rangle\langle i|$ is dephasing in a chosen basis
- ➜ Basis dependent measure!!
- Mathematically,

$$W_{\Pi_b}(\rho) \leq \max_{I \geq \Pi_b \geq 0} \mathrm{Tr}[\Pi_b(\rho - \Gamma \circ \rho)] = \mathrm{Tr}|\rho - \Gamma \circ \rho| \equiv C_{NSIT}(\rho)$$

- Dephasing covariant operations [Meznaric/Clark/AD, PRL **110**, 070502 (2013)]
- Related to resource theory of coherence

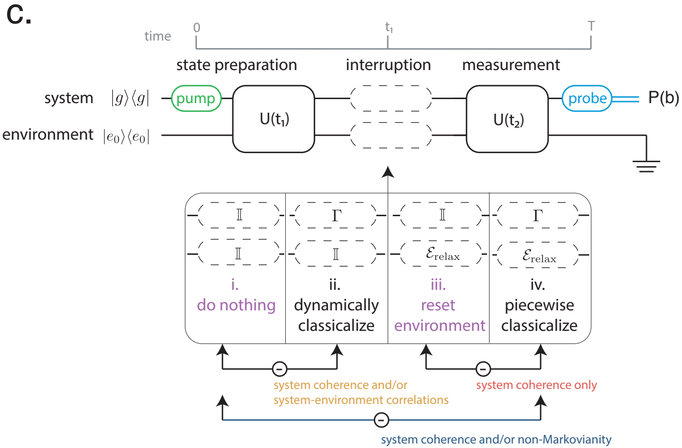
[Baumgratz/Cramer/Plenio, PRL **113**, 140401 (2014)] [Marvian/Spekkens, PRA **94**, 052324 (2016)]

[Streltsov, Rana, Adesso, Winter, Eisert, Parashar, ...]

NSIT

- $0 \leq C_{NSIT}(\rho) \leq 1 - \frac{1}{d}$
- We will only use the witness $W_{\Pi_b}(\rho)$

NSIT without system-bath separation



Why do all this?

- Is EET quantum? Ultrafast spectroscopy experiment proposal
- Quantumness of processes not states

  Meznaric/Clark/AD, PRL **110**, 070502 (2013)
- Quantumness where system-bath isolation is impossible
- Quantumness in macroscopic scenarios
- Extracting quantumness directly from spectroscopy
- Most light-matter interactions - trapped ions, superconducting qubits are studied spectroscopically

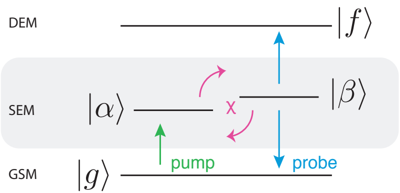
Work in progess

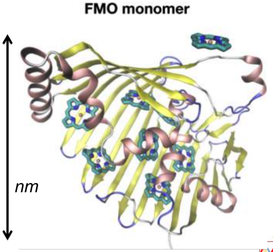
Light-matter interaction

$$H = H_0 + V(\boldsymbol{r}, t)$$

Matter: System & bath (quantum)

$$H_0 = \underbrace{\sum_i \epsilon_i |i\rangle\langle i| + \sum_{m \neq n} V_{mn} |m\rangle\langle n|}_{H_S} + \underbrace{\hbar \sum_j \Omega_j a_j^\dagger a_j}_{H_B} + \underbrace{\sum_j g_j |j\rangle\langle j| (b_j^\dagger + b_j)}_{H_{SB}}$$

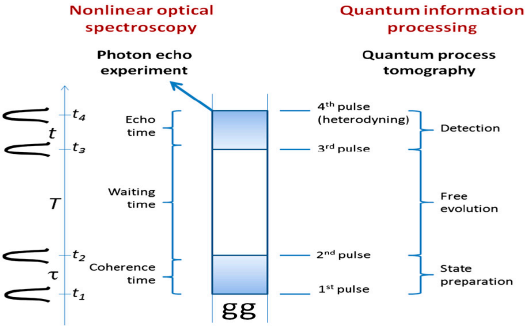




Light: classical

$$V(\boldsymbol{r}, t) = -\boldsymbol{\mu} \cdot \boldsymbol{E}(\boldsymbol{r}, t)$$

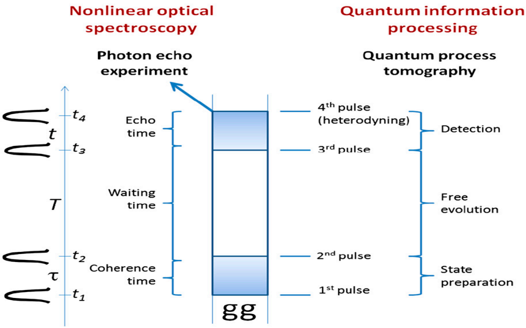
- $\boldsymbol{E}(\boldsymbol{r},t) = \sum_{n=1}^{N} \underbrace{E_n(t-t_n)}_{\eta \frac{e^{-t^2/2\sigma_n^2} e^{i\omega_n t}}{\sqrt{2\pi\sigma_n^2}}} e^{i(\boldsymbol{k}_n \cdot \boldsymbol{r} + \phi_n)} \boldsymbol{e}_n$
- Choosing pulse parameters can give various spectroscopies
- Transient absorption, circular dichroism, photon echo etc.
- 4-wave mixing can give full process tomography on SEM



Aspuru-Guzik group

Spectroscopy

- 4-wave mixing can give full process tomography on SEM

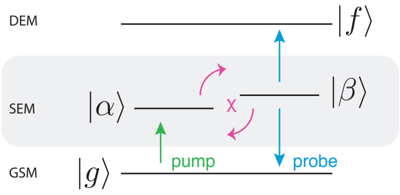


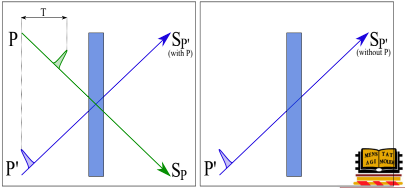
Aspuru-Guzik group

- ✘ QPT implicitly assumes quantum mechanics
  ✘ Requires at least $d^4 - d^2$ experiments
  - System dimension unclear

Pump-probe spectroscopy

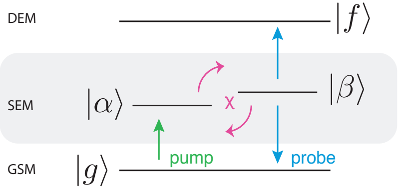
- We use pump-probe: $N = 2$ and $\phi = \phi_1 = \phi_2$,
- $\rho_{ij}(T) = \chi_{ijkl}\rho_{kl}(0)$, χ is a map
- Ability of χ to generate coherence in the energy basis?
- Pump prepares a superposition state ρ
- Probe rotates the basis to make a measurement





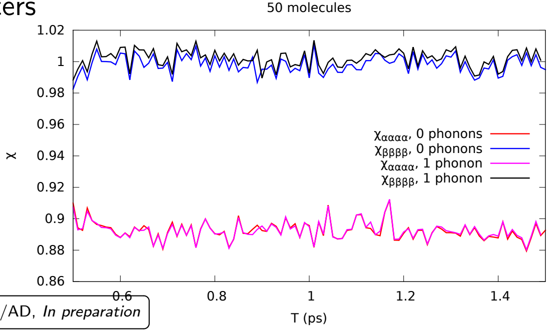
(a) (b)

Knee/Marcus/Smith/AD, *In preparation*



- χ is 4×4
- After assumptions (trace-preservation), 12 independent parameters

Yuen-Zhou, *et al.*, PNAS **108**, 17615-17620 (2011)

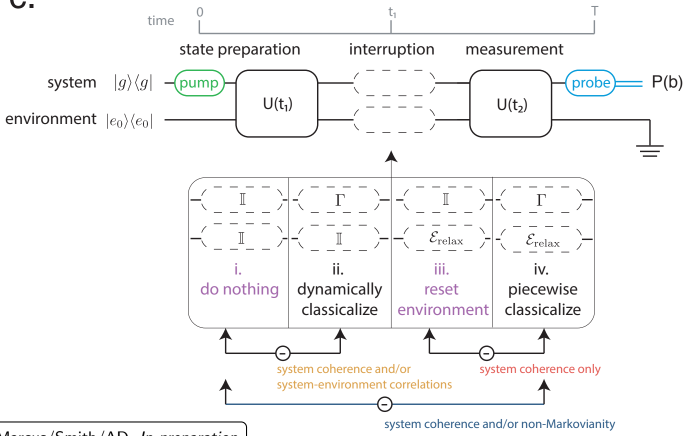


Knee/Marcus/Smith/AD, *In preparation*

Pump-probe spectroscopy

- Let us target $|\alpha\rangle$ for both pump and probe
- (ii) requires additional pulses
- (iv) Population tomography and selective repreparation at t_1. Then, $P^{(iv)}(b) = \sum_j \chi_{\alpha\alpha jj}(T - t_1)\chi_{jj\alpha\alpha}(t_1)$

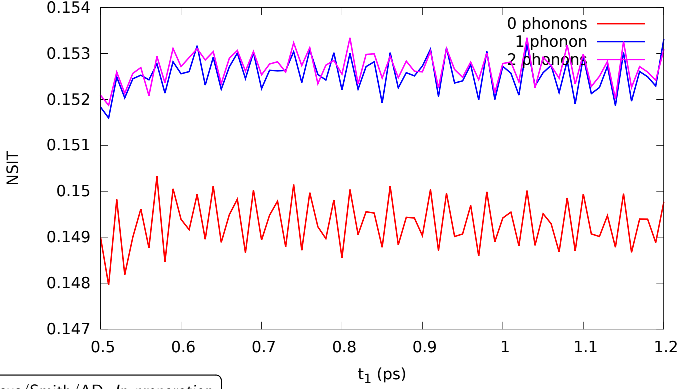
c.



Knee/Marcus/Smith/AD, *In preparation*

Pump-probe spectroscopy

- $P^{(iii)}(b) - P^{(iv)}(b)$: System coherence only
- $P^{(i)}(b) - P^{(iv)}(b)$: System coherence + bath Markovianity
- $P^{(i)}(b) - P^{(iii)}(b)$: System coherence + system-bath correlations



Knee/Marcus/Smith/AD, *In preparation*

Why do all this?

- Is EET quantum? In progress ...

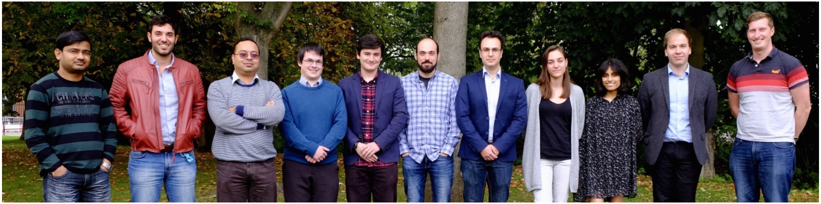
- Extracting quantumness directly from spectroscopy
- Most light-matter interactions - trapped ions, superconducting qubits are studied spectroscopically

- Quantumness where system-bath isolation is impossible

- Quantumness in macroscopic scenarios

- Quantumness of processes not states

Us



- Magdalena Szczykulska
- Dominic Branford
- Samuele Ferracin
- Jamie Friel
- Evangelia Bisketzi
- Christos Gagatsos
- George Knee
- Theodoros Kapourniotis
- Max Marcus

www.warwick.ac.uk/qinfo