

Quantum dynamics and biomolecular function

Ross McKenzie



Outline

- What is biological physics?
- Optically active biomolecules as complex quantum systems
- A minimal model quantum many-body Hamiltonian
- Observing the “collapse” of the quantum mechanical wavefunction!
- International Institute for Complex Adaptive Matter

Biophysics or **Biological Physics**?

- Biophysical community is mostly concerned with using well-established physical techniques to better understand biological systems. Most members are not in physics departments.
- **Biological Physics** concerns studying biological systems as interesting complex physical systems in their own right, with an emphasis on discovering unifying principles.

Biological physics

“Ask not what physics can do for biology, ask what biology can do for physics”
Stan Ulam

Frauenfelder, Wolynes, Austin
Rev. Mod. Phys. 71, S419 (1999)

See also, J. Knight, Nature 419, 244 (2002)

Cross-cultural issues: Specificity vs. universality

For complex biomolecular materials when do the details matter?

- Physicists say the details don't matter. They think cows are spherical!
- Chemists say details do matter.
- Biologists say the details are a matter of life and death!
- But, the same model in quantum many-body physics can describe magnetic impurities in metals, electronic transport through quantum dots, and single molecule transistors.

Some key questions concerning biomolecular functionality

Which **details** matter?

- What role does **water** play?
- Do biomolecules have the optimum structure to exploit **dynamics** for their functionality?
- When is **quantum** dynamics (e.g., tunneling, coherence) necessary for functionality?

Scientific challenges for new technologies (& ARC National Priorities)

At atomic and molecular level need to understand:

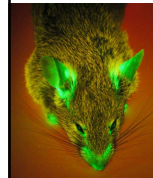
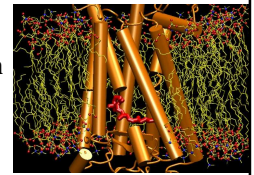
- Charge transport and separation (electrons and protons)
- Energy conversion (transduction); e.g, light -> chemical energy
- Energy transport and storage
- Selective breaking and making chemical bonds (catalysis)

Biomolecules do these very well!!

Why should **nanotechnologists** be interested in biomolecules?

Photo-active biomolecules are the ultimate nanoscale devices

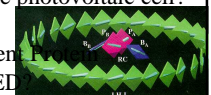
Retinal & rhodopsin
-ultimate photo-activated mechanical switch?



Photosynthetic light harvesting complexes

- the ultimate photovoltaic cell?

Green Fluorescent Protein
-the ultimate LED



Device design by Biomimetics

Biomolecular systems have features nanotechnologists dream to mimic:

- High speed, efficiency, and selectivity
- Synthesis and self-assembly of complex molecular nanostructures
- Fine tuning by molecular engineering
- High quantum efficiency
- Durability & self-repair

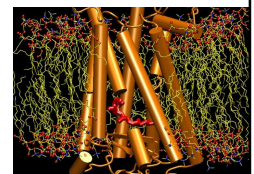
Ref: ``Approaches for biological and biomimetic energy conversion,`` PNAS 103, 5251 (2006).

Why should **biologists** be interested in **quantum physics**?

It is responsible for the functionality of

Photo-active biomolecules

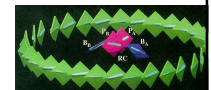
- **Retinal**, responsible for vision
-signal transduction
(photon -> conformational change -> electrical signal)



Photosynthetic Light harvesting complexes

-Energy transfer and transduction

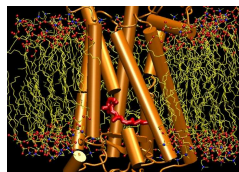
Green Fluorescent Protein
- Powerful marker



Why should **quantum physicists** be interested in biomolecules?

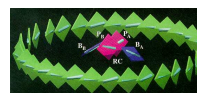
Photo-active biomolecules are tuneable systems at the quantum-classical boundary

- **Retinal**, responsible for vision
- Single photon detector
- Quantum dynamics when the Born-Oppenheimer approx. breaks down
- Entanglement of electrons & nuclei
- Effect of decoherence on Berry's phase

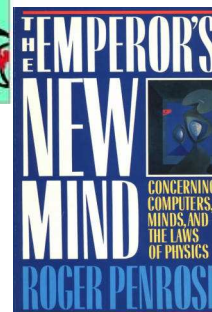
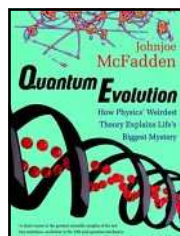


Photosynthetic Light harvesting complexes

Quantum coherence over large distances?



Quantum biology at amazon.com?



LETTERS

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^{1,4} & Graham R. Fleming^{1,2}

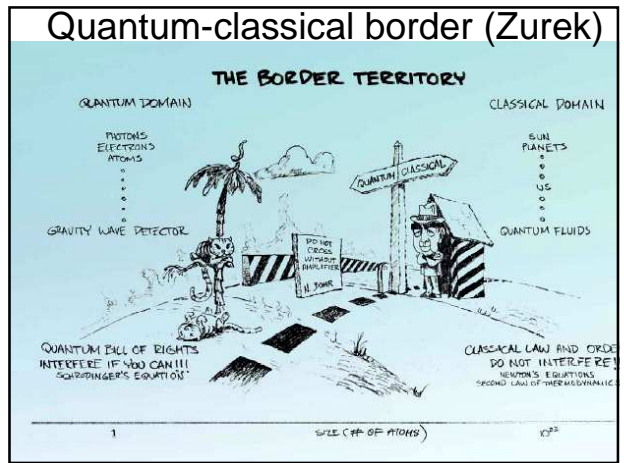
Electronic energy delocalization and dissipation in single- and double-stranded DNA

Ivan Buchvarov, Qiang Wang, Milen Raytchev, Anton Trifonov, and Torsten Fiebig*

Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Edited by Esther M. Conwell, University of Rochester, Rochester, NY, and approved January 17, 2007 (received for review August 4, 2006)

The mechanism that nature applies to dissipate excess energy from solar UV light absorption in DNA is fundamental, because its efficiency determines the vulnerability of all genetic material to photodamage and subsequent mutations. Using femtosecond time-resolved broadband spectroscopy, we have traced the electronic excitation in both time and space along the base stack in a series of single-stranded and double-stranded DNA oligonucleotides. The obtained results demonstrate not only the presence of delocalized electronic domains (excitons) as a result of UV light absorption, but also reveal the spatial extent of the excitons. Several years ago, we (16) reported spectroscopic electronic delocalization in double-stranded of that contained pairs of a fluorescent DNA base present study, we investigated natural single-str (dA)_n [composed of n = 2, 3, 4, 5, 6, 12, 15, 1 2'-deoxyadenosine (dA) residues, respectively], a hic-stranded oligonucleotides (dA)_n(dT)_n (n = (dAT)_n(dAT)_n). The single-stranded homonucleotides were chosen because of their reported helical structure in aqueous solutions and the option to



A complex quantum system :Photo-active yellow protein

Quantum system =
Ground + electronic
Excited state of
Chromophore

Environment =
Protein +
Water bound to
Protein +
Bulk water

The quantum measurement problem

- Schrodinger's cat is dead and alive at the same time! Only when we look does it become one or the other.

``Collapse'' of the wave function

- Zurek (1982), Joos and Zeh (1985)
- Environment causes decay of the off-diagonal density matrix elements (decoherence)
- ``Collapse'' occurs due to continuous ``measurement'' of the state of the system by the environment.
- What is the relevant time scale?

M. Schlosshauer, Rev. Mod. Phys. (2004)

Seeking a minimal model for this quantum system and its environment

- Must capture and give insights into essential physics.
- Tells us which physical parameters lead to qualitative changes in quantum dynamics.

Independent boson model Hamiltonian

$$H = \frac{1}{2}\epsilon\sigma_z + \sum_{\beta} \omega_{\beta} a_{\beta}^{\dagger} a_{\beta} + \sigma_z \sum_{\beta} C_{\beta} (a_{\beta} + a_{\beta}^{\dagger})$$

- Chromophore is **two level system (TLS)**.
- **The environment** is modelled as an infinite bath of harmonic oscillators.
- Effect of environment on quantum dynamics of TLS is completely determined by the **spectral density**:

$$J(\omega) = \frac{4\pi}{\hbar} \sum_{\beta} C_{\beta}^2 \delta(\omega - \omega_{\beta})$$

Quantum dynamics of TLS

TLS is initially in a coherent superposition state uncoupled from the bath. Reduced density matrix

$$\rho_{11}(t) = \rho_{11}(0) = |a|^2$$

$$\rho_{22}(t) = \rho_{22}(0) = |b|^2 = 1 - \rho_{11}(0)$$

$$\rho_{12}(t) = \rho_{21}^*(t) = a^* b \exp(-i\epsilon t + i\theta(t) - \Gamma(t, T))$$

Decay of coherence

$$\Gamma(t, T) = \int_0^{\infty} d\omega J(\omega) \coth\left(\frac{\omega}{2k_B T}\right) \frac{(1 - \cos \omega t)}{\omega^2}$$

Spectral diffusion

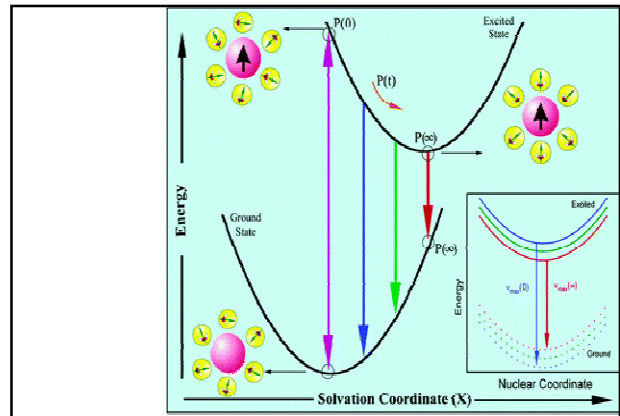
$$\nu(t) = \epsilon - \frac{d\theta(t)}{dt} = \epsilon - E_R - \int_0^{\infty} d\omega \frac{J(\omega)}{\omega} \cos(\omega t)$$

Spectral density can be extracted from ultra-fast laser spectroscopy

- Measure the time dependence of the frequency of maximum fluorescence (dynamic Stokes shift)

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} = \int \frac{J(\omega)}{\omega} \cos(\omega t) d\omega$$

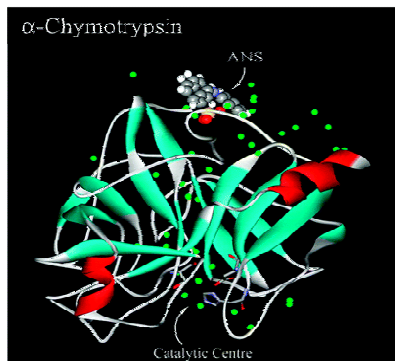
- Data can be fit to multiple exponentials.
- Fourier transform gives spectral density!



Pal and Zewail, Chem. Rev. (2004)

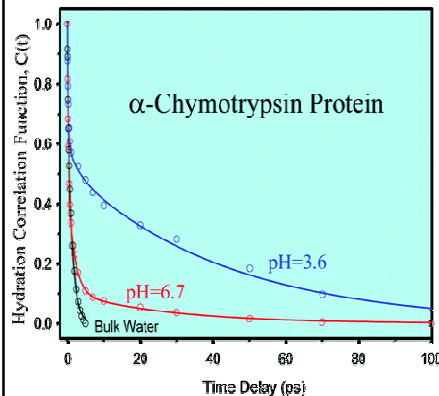
An example

- ANS is chromophore



Pal, Peon, Zewail, PNAS (2002)

Femtosecond laser spectroscopy: Measurement of the time-dependent spectral shift of a chromophore in a solvated protein



Increasing pH unfolds (denatures) protein and exposes chromophore to more solvent.

Presence of protein reduces psec relaxation and adds ~50 psec relaxation.

Pal, Peon, Zewail, PNAS (2002)

Measured spectral densities

$$J(\omega) = \frac{\alpha_p \omega}{1 + (\omega \tau_p)^2} + \frac{\alpha_b \omega}{1 + (\omega \tau_b)^2} + \frac{\alpha_s \omega}{1 + (\omega \tau_s)^2}$$

Three contributions of ohmic form

• Bulk water (solvent)

$$\alpha_s \sim 1-10 \quad \tau_s \sim 0.3-3 \text{ psec}$$

• Water bound to the protein, esp. at surface

$$\alpha_b \sim 10-100 \quad \tau_b \sim 10-100 \text{ psec}$$

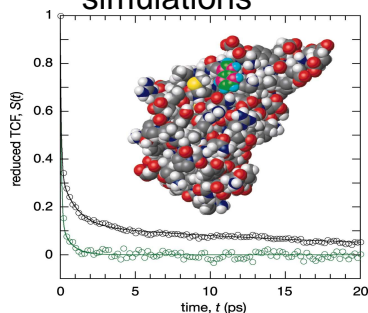
• Protein

$$\alpha_p \sim 100-1000 \quad \tau_p \sim 1-100 \text{ nsec}$$

Spectral density for diverse range of biomolecules & solvents

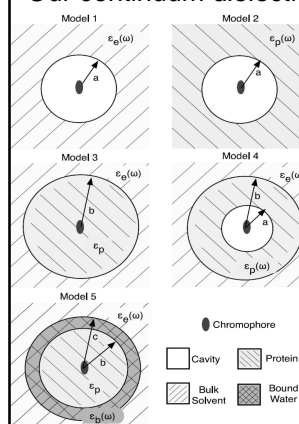
| Chromophore | Protein | Solvent | Ref. | E_R (cm ⁻¹) | A_1, τ_1 | A_2, τ_2 | A_3, τ_3 |
|--------------|----------------|--------------|------|---------------------------|----------------|----------------|-----------------|
| Trp | none | water | [82] | 0.65, 160 fsec | 0.35, 1.1 psec | | |
| Trp | none | water | [5] | 2193 | 0.55, 340 fsec | 0.45, 1.6 psec | |
| Trp | SC | buffer | [83] | 1440 | 0.6, 800 fsec | 0.4, 38 psec | |
| Trp | Monellin | Buffer | [37] | 960 | 0.46, 1.3 psec | 0.54, 16 psec | |
| Trp | SNase-WT | Buffer | [3] | 850 | 0.46, 5 psec | 0.54, 153 psec | |
| Trp | SNase-K110A | Buffer | [3] | 876 | 0.77, 3 psec | 0.23, 96 psec | |
| Trp | HSA | water, pH 7 | [4] | 1156 | 0.39, 5 psec | 0.61, 133 psec | |
| Trp | HSA | water, pH 9 | [4] | 1015 | 0.3, 1.6 psec | 0.7, 46 psec | |
| Dansyl | SC | water | [83] | 1180 | 0.94, 1.5 psec | 0.06, 40 psec | |
| DCM | HSA | Tris buffer | [84] | 515 | | 0.25, 600 psec | 0.75, 10 nsec |
| Prodan | none | buffer | [85] | 2313 | 0.47, 130 fsec | 0.53, 770 fsec | |
| Prodan | HSA | buffer | [85] | 916 | 0.19, 780 fsec | 0.56, 2.6 psec | 0.25, 32 psec |
| Prodan | HSA | buffer | [85] | 1680 | 0.23, 710 fsec | 0.41, 3.7 psec | 0.36, 57 psec |
| Acrylodan | HSA | 0.2M Gdn.HCl | [85] | | 0.16, 280 fsec | 0.36, 5.4 psec | 0.48, 61 psec |
| Acrylodan | HSA | 0.6M Gdn.HCl | [85] | | 0.2, 120 fsec | 0.55, 2 psec | 0.25, 13.5 psec |
| MPTS | none | buffer | [86] | 2097 | 0.8, 20 fsec | 0.2, 340 fsec | |
| MPTS | AlbCS | buffer | [86] | 1910 | 0.85, 33 fsec | 0.1, 2 psec | 0.05, 67 psec |
| bis-ANS | GluRS (native) | water | [38] | 739 | | 0.45, 170 psec | 0.55, 2.4 nsec |
| bis-ANS | GluRS (molten) | urea | [38] | 500 | | 0.63, 60 psec | 0.37, 0.96 nsec |
| 4-AP | GluRS (native) | water | [38] | 1330 | | 0.85, 40 psec | 0.15, 58 psec |
| 4-AP | GluRS (molten) | urea | [38] | 700 | | 0.77, 50 psec | 0.23, 0.9 nsec |
| Zn-porphyrin | Cytochrome-c | water | [9] | 170 | | 0.4, 250 psec | 0.6, 1.5 nsec |

Classical molecular dynamics simulations



C(t) for Trp (green) and Trp-3 in monellin (black) in aqueous solution at 300 K Nilsson and Halle, PNAS (2005).

Our continuum dielectric models for environment



- We have calculated $J(\omega)$ for 5 models for environment
- Key feature is separation of time and distance scales: Protein much larger than chromophore
- Relaxation time of Protein \gg Bound water \gg Bulk solvent

What have we learned?

- We can completely characterise the system-environment interaction for biological chromophores.
- The known spectral densities can be used to make definitive statements about the importance of quantum effects in biomolecular processes.
- Due to their tuneable coupling to their environment biomolecular systems may be model systems to use to test ideas in quantum measurement theory.
- For chromophores the timescale of the "collapse" is less than 100 fsec.

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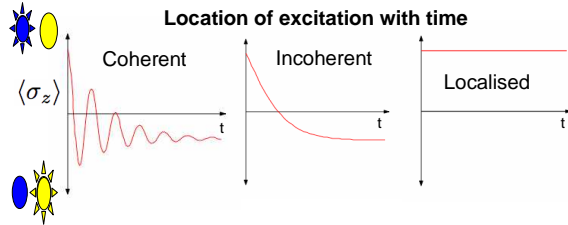
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Criteria for quantum coherent transfer of excitation energy between two chromophores

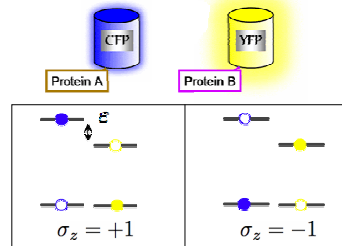
J. Gilmore & RHM, Chem. Phys. Lett. (2006)



Realisation of spin-boson model for coupled chromophores

$$H = \frac{1}{2} \varepsilon \sigma_z + \Delta \sigma_x + \sum_{\beta} \sigma_z M_{\beta} (a_{\beta}^{\dagger} + a_{\beta}) + \sum_{\beta} \omega_{\beta} a_{\beta}^{\dagger} a_{\beta}$$

What is the two level system?



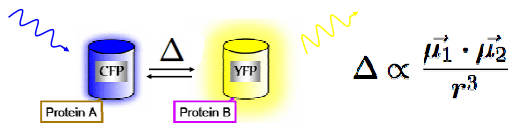
- Excitation can be on either of two molecules
- Each two energy levels

If only one excitation is present, effectively a **two level system**

Realisation of spin-boson model for coupled chromophores

$$H = \frac{1}{2} \varepsilon \sigma_z + \Delta \sigma_x + \sum_{\beta} \sigma_z M_{\beta} (a_{\beta}^{\dagger} + a_{\beta}) + \sum_{\beta} \omega_{\beta} a_{\beta}^{\dagger} a_{\beta}$$

What is Δ , the coupling?



- Excitations may be transferred by **dipole-dipole** interactions
 - Shine in blue, get out yellow!
 - Basis of **F**luorescent **R**esonant **E**nergy **T**ransfer (FRET) spectroscopy
 - Used in photosynthesis to move excitations around



International Institute for Complex Adaptive Matter

www.i2cam.org

One of 5 International Materials Institutes supported by US National Science Foundation (approx. US\$3.5M over 5 years)

- 30 plus Member Universities
- Focus on biological physics and correlated electron materials
- Multi-disciplinary and anti-reductionist in approach



International Institute for Complex Adaptive Matter

- U. Queensland is the first Australian branch campus
- Branch Membership costs US\$10K per year

Members of branch campuses can apply for funds for

- Junior Travel awards for international collaboration
- Postdoctoral Fellowships
- To host Exploratory Workshops

An I2CAM Exploratory Workshop
"Quantum Dynamics and Biomolecular Function"
 Rydges Capricorn Resort, Yeppoon,
 Qld, Australia
 9-13 April 2007

www.physics.uq.edu.au/i2camworkshop
 See especially the readings



THE UNIVERSITY OF QUEENSLAND

Invited Speakers:
 Dan Cox, UC Davis
 Samir Kumar Pal, Bose Centre, India
 Minhaeng Cho, Korea University
 Ken Ghiggino, Melbourne
 Shigehiko Hayashi, Kyoto
 Wendel Wohlleben, Marburg
 Dong Ping Zhong, Ohio State
 His-Sheng Goan, Taiwan
 Paul Burn, University of Qld
 Seth Olsen, University of Qld
 Alan Mark, University of Qld
 Paul Meredith, University of Qld



Some possible key areas to invest in

- Understand biomolecular dynamics, esp. protein folding, using time-resolved x-ray scattering.
- Using x-ray and/or neutron scattering to understand structure of solvated amino acids and/or location of protons and water in biomolecular structures.
- Understand hydration dynamics with femtosecond laser spectroscopy.
- ``Statistical mechanical'' modelling of protein-protein interactions and gene switching.