Quantum decoherence of electronic excited states in biomolecules

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The University Of Queensland
AUSTRALIA

Australian Government
Australian Research Council

I2CAM International Institute for Complex Adaptive Matter

Outline

- Optically active biomolecules are complex systems at the quantum-classical boundary
- An effective Hamiltonian for quantum decoherence of optically excited states
- Spectral density for chromophore-environment interaction is well characterised and can be described by dielectric continuum models.
- The ``collapse'' of the wavefunction occurs in tens of fsec
- Ref: J. Gilmore and RHM, J. Phys. Chem. A 112, 2162 (2008) [Review article]

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Quantum control of processes in large molecules in condensed phases

- What are the relevant length and time scales for coherence?
  10-100's fsec
- What is the main physical source of decoherence?
  dielectric relaxation of the environment
- Can we learn something about biomolecular processes and function?

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Quantum biology at amazon.com?

Engaging with Hameroff & Penrose

PNAS

Weak, strong, and coherent regimes of Fröhlich condensation and their applications to terahertz medicine and quantum consciousness

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PHYSICAL REVIEW E **80**, 021912 (2009)

Penrose-Hameroff orchestrated objective-reduction proposal for human consciousne is not biologically feasible

Laura K. McKemmish,[1] Jeffrey R. Reimers,[1,*] Ross H. McKenzie,[2] Alan E. Mark,[3] and Noel S. Hush[4]
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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[3,4] & Graham R. Fleming[1,2]

PNAS

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

Ivan Buchvarov, Qiang Wang, Milen
Eugene F. Merkert Chemistry Center, Boston C

Edited by Esther M. Conwell, University of Roch

The mechanism that nature applies to dis solar UV light absorption in DNA is f efficiency determines the vulnerability photodamage and subsequent mutati time-resolved broadband spectroscopy, tronic excitation in both time and space series of single-stranded and double-st tides. The obtained results demonstrate delocalized electronic domains (excitons absorption, but also reveal the spatial e

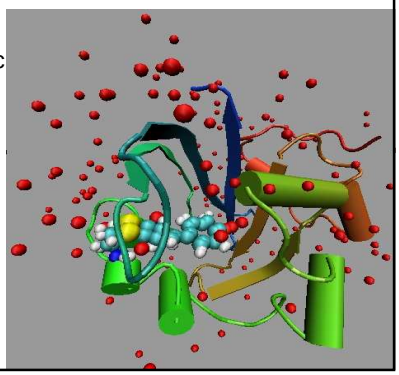
Coherence Dynamics i Photosynthesis: Protein of Excitonic Coherence

Hohjai Lee, Yuan-Chung Cheng, Graham R. Fleming*

A complex quantum system: Photo-active yellow protein

Quantum system = Ground + electronic excited state of chromophore

Environment = Protein + Water bound to Protein + Bulk water



Seeking a minimal model for this quantum system and its environment

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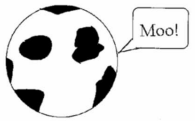
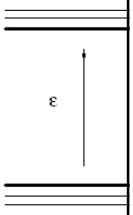


- Must capture and give insights into essential physics.
- Tells us which physical parameters lead to qualitative changes in quantum dynamics.

- Model chromophore as a two level system (TLS)
- Use Pauli matrix σ_z to describe the two states, ground state and excited state
- The Hamiltonian is

$$H_{TLS} = \frac{1}{2}\epsilon\sigma_z$$



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).
- **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**:

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

Key ideas from Leggett

- We don't need to know all the microscopic details of the environment, nor its interaction with the system. Only need J(ω).
- Spectral density can be determined from measurements of the classical dynamics.
- Many spectral densities are ``ohmic'', i.e., J(ω) ≈ $\alpha\,\omega$ for $\omega < 1/\tau$
  τ is relaxation time of the bath.
- For $\alpha > 1$ quantum dynamics is incoherent.

Caldeira and Leggett, Ann. Phys. (1983); Leggett, J. Phys.: Cond. Matt. (2002).

Quantum dynamics of two-level system

Suppose qubit is initially in a coherent superposition state $|\Psi> = a|1> + b|2>$ uncoupled from the bath.

Reduced density matrix can be evaluated exactly (no Markovian or Born approximation)

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

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

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

gives decoherence and spectral diffusion in terms of J(ω)

Quantum dynamics of two-level system determined by J(ω)

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

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

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

``Collapse'' of the wave function

- Zurek (`82), Joos and Zeh (`85), Unruh (`89)
- 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 for these biomolecules?

~ 100 fsec

Timescale for decoherence

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

$$\frac{\hbar}{\tau_g} = \sqrt{2E_R k_B T}$$

~ 1 / 100 fsec

$$E_R = \int_0^\infty d\omega \frac{J(\omega)}{\omega}$$

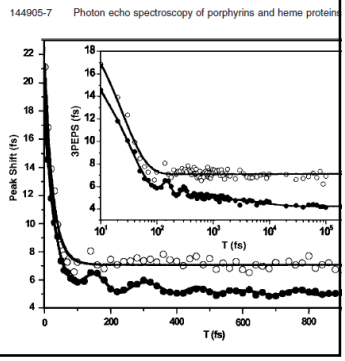
Re-organisation energy of environment

Observing the collapse of the wave function with photo-echo spectroscopy

Peak shift vs. time

$$S(t) = \frac{\tau_g}{\sqrt{\pi}} C(t)$$

J. Chem. Phys. 124, 144905 (2006)



Complementary methods to extract the spectral density

- Femtosecond laser spectroscopy
- Molecular dynamics simulations
- Continuum dielectric models

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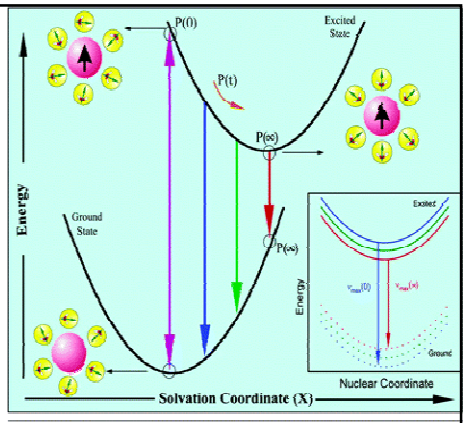
Spectral density can be extracted from femtosecond laser spectroscopy

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

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

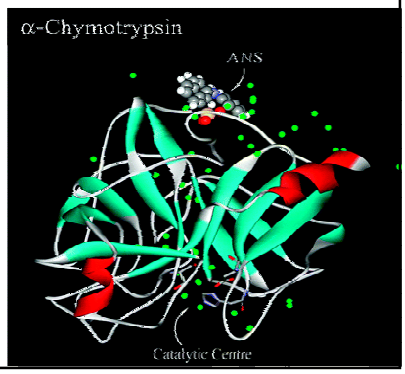
- Data can be fit to multiple exponentials.
- Fourier transform gives spectral density!



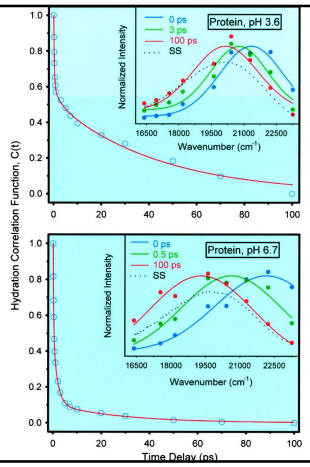
Pal and Zewail, Chem. Rev. (2004)

An example

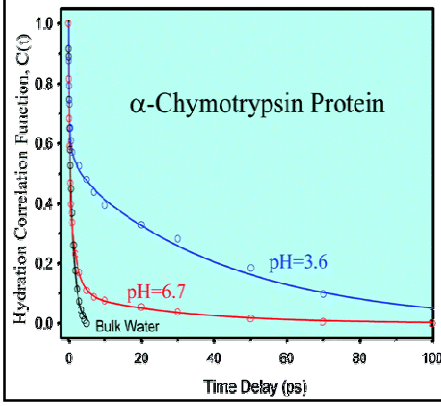
- ANS is chromophore



Pal, Peon, Zewail, PNAS (2002)



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)

α_s ~ 1–10 τ_s ~ 0.3-3 psec

•Water bound to the protein, esp. at surface

α_b ~ 10-100 τ_b ~ 10-100 psec

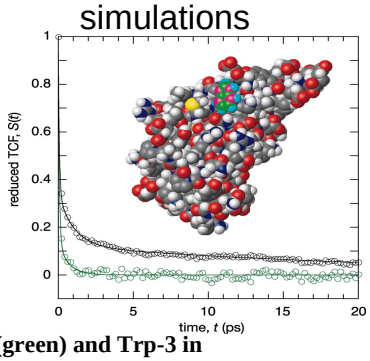
•Protein

α_p~ 100–1000 τ_p ~ 1-100 nsec

Spectral density for diverse range of biomolecules & solvents

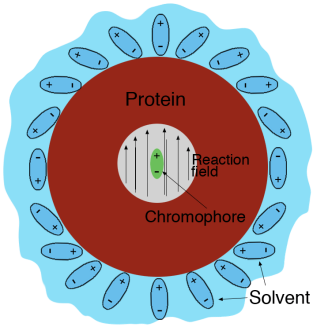
Chromophore	Protein	Solvent	Ref.	E_R (cm^{-1})	A_1, τ_1	A_2, τ_2	A_3, τ_3
Trp	none	water	[82]		0.65, 160 fsec	0.35, 1.1 psec	
Trp	none	water	[5]	2193	0.55, 340 fsec	0.45, 1.6 psec	
Trp	SC	buffer	[83]	1440	0.6, 800 fsec	0.4, 38 psec	
Trp	Monellin	Buffer	[37]	960	0.46,1.3 psec	0.54, 16 psec	
Trp	SNase-WT	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
Acrylodan	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	Ab6C8	buffer	[86]	1910	0.85, 33 fsec	0.1, 2 psec	0.05, 67 psec
bis-ANS	GlnRS (native)	water	[38]	750		0.45, 170 psec	0.55, 2.4 nsec
bis-ANS	GlnRS (molten)	urea	[38]	500		0.63, 60 psec	0.37, 0.96 nsec
4-AP	GlnRS (native)	water	[38]	1330		0.85, 40 psec	0.15, 580 psec
4-AP	GlnRS (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).

Modelling interaction of chromophore with environment

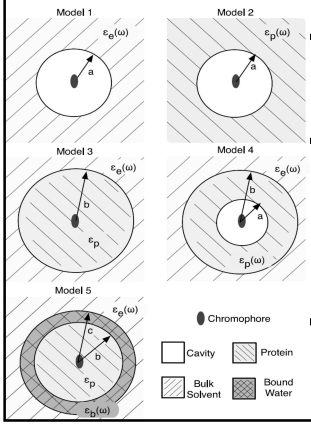


- The solvent forms a polarised cage around the solute (chromophore) dipole
- The resulting electric field (the reaction field **R)** interacts with the solute dipole μ
- This lowers the total energy, and makes solvation favourable.

$$\Delta E = -\vec{\mu} \cdot \vec{R}$$

- Based on the Onsager model of solvation (1936)

Our continuum dielectric models for environment



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

Key physics behind decoherence

- Most chromophores have a large difference between electric dipole moment of ground and excited states.
- Water is a very polar solvent (static dielectric constant ε_s = 80)
  - Water molecules have a net electric dipole moment
  - Dipole direction fluctuates due to thermal fluctuations (typical relaxation time at 300K is ~1 psec)
- Chromophore experiences fluctuating electric fie
- Surrounding protein does not completely shield chromophore from solvent.

Spectral density determined by dielectric relaxation of environment

$$J_1(\omega) = \frac{(\Delta\mu)^2}{2\pi\epsilon_0 a^3} \,\mathrm{Im}\, \frac{(\epsilon_s(\omega) - \epsilon_c)}{2\epsilon_s(\omega) + \epsilon_c}$$

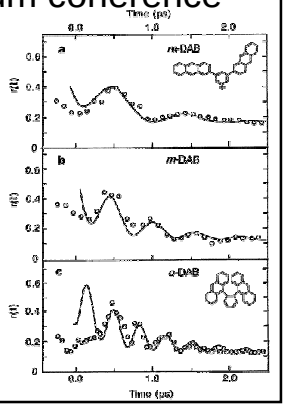
ε(ω) = frequency-dependent dielectric function
Δμ = difference between dipole moment of ground and exctied states
a = cavity radius

Criteria for quantum coherence

``Observation of Quantum Coherence for Recurrence Motion of Exciton in Anthracene Dimers in Solution''

I. Yamazaki et al., J. Am. Chem. Soc. 125, 7192 (2003)

However, for relevant parameters we find quantum coherence is impossible! Gilmore & RHM, *Chem. Phys. Lett.* 421, 266 (2006).



Conclusions

- Biomolecules function in a hot wet environment
- Spectral density characterises quantum system-environment (protein+ water) interaction for biomolecular chromophores.
- These spectral densities quantify electronic coherences and give decoherence timescales of order 100 fsec.

J. Gilmore and RHM, J. Phys. Chem. A 112, 2162 (2008)
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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, entanglement) necessary for functionality?

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Specificity vs. universality

For complex molecular 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!

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Kauzmann's maxim

- Walter Kauzmann (1916-2009) was first to understand the hydrophobic interaction
- "people will tend to believe what they want to believe rather than what the evidence before them suggests they should believe"

Reminiscences of a life in protein physical chemistry, *Protein Science* 2, 671 (1992)

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The environment matters!

Fluorescence from different sites within protein

Cohen et al.,
Science
296, 1700 (2002)