Signatures of Quantum Behaviour in Phonon-Driven Energy Transport

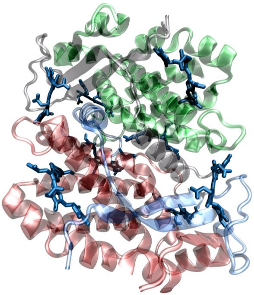
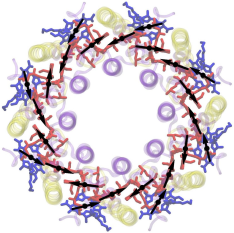
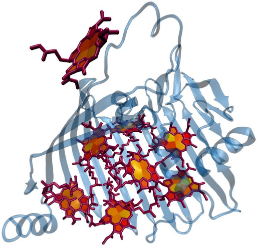
Edward O'Reilly
Alexandra Olaya-Castro *Avinash Kolli*

(University College London)

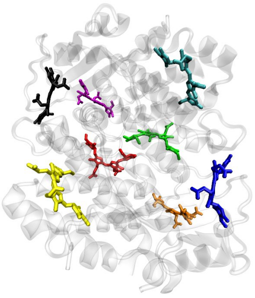
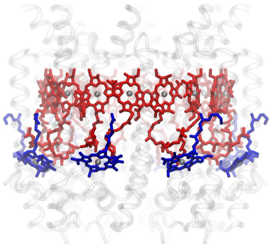
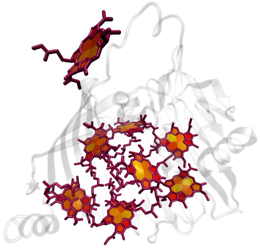
NPCQS2012

23 April 2012

Light Harvesting Complexes

Marine Algae	Purple Bacteria	Green Sulphur Bacteria
		
PE545 (PC645) E.Collini *et.al.* Nature 2010 (180K) C.Wong *et.al.* Nature Chem 2012 (300K)	LH2 E.Harel *et. al.* PNAS 2012 (300K)	FMO G.S. Engel *et.al.* Nature 2007 (77K) Panitchayangkoon *et.al.* PNAS 2010 (277K)

Light Harvesting Complexes

Marine Algae	Purple Bacteria	Green Sulphur Bacteria
		
PE545 (PC645) E.Collini *et.al.* Nature 2010 (180K) C.Wong *et.al.* Nature Chem 2012 (300K)	LH2 E.Harel *et. al.* PNAS 2012 (300K)	FMO G.S. Engel *et.al.* Nature 2007 (77K) Panitchayangkoon *et.al.* PNAS 2010 (277K)

Motivation

Key Questions:

- Role of long lived excitonic coherences?
- Influence of high energy vibrational modes?
  - vibrational coherences
    - Richards *et.al.* PhysChemLett. 2012, Turner *et.al.* PCCP 2012
  - in models of olfaction
    - Turin Chem Senses. 1996 , Brookes *et.al.* PRL 2007 , Franco *et.al.* PNAS 2011
  - in enzyme catayzed reactions
    - Hay *et.al.* Nature Chemistry 2012

Outline

1. Theoretical approach
2. Result: Optimal transport corresponds to non-classical behaviour of vibrational modes

Theoretical Framework

System: Pigments/Electronic dof;

$$H_{el} = \sum_m \epsilon_m \sigma_m^+ \sigma_m^- + \sum_{m,n>m} V_{mn}(\sigma_m^+ \sigma_n^- + \sigma_n^+ \sigma_m^-) = \sum_M E_M \left|M\right\rangle \left\langle M\right|$$

Bath: Protein & solvent vibrational dof;

$$H_B = \sum_k \omega_k b_k^\dagger b_k$$

Interaction:

$$H_{SB} = \sum_{m,k} \mathcal{V}_m \otimes B_k = \sum_{m,k} g_{k,m} \sigma_m^+ \sigma_m^- \otimes (b_k^\dagger + b_k)$$

Spectral density:

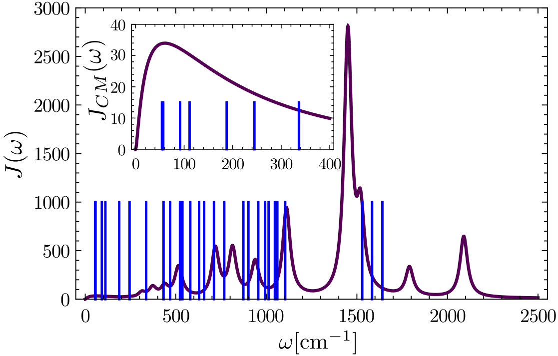
$$J_m(\omega) = \sum_k g_{k,m}^2 \delta(\omega - \omega_k), \qquad \lambda_m = \int_0^\infty \frac{J_m(\omega)}{\omega} \mathrm{d}\omega$$

Independent (uncorrelated) and identical baths at each site: $J_m(\omega) = J(\omega)$

Spectral Density

Two components

- Continuous distribution of modes with $\omega_k \leq k_B T$
- High energy quantised vibrations $\omega_k \gg k_B T$



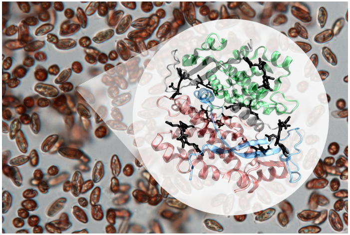
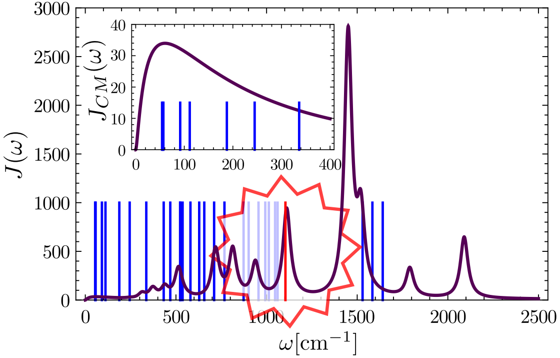


Image: E.J.O (Recharge magazine Feb 2012)

Spectral Density

Two components

- Continuous distribution of modes with $\omega_k \leq k_B T$
- High energy quantised vibrations $\omega_k \gg k_B T$



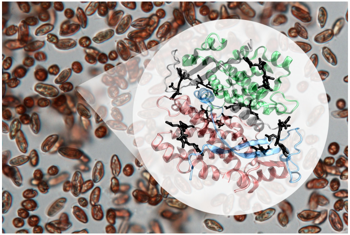
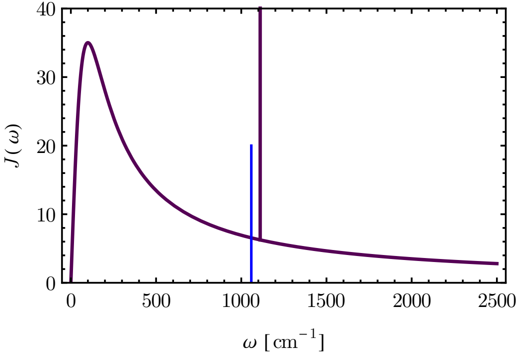


Image: E.J.O (Recharge magazine Feb 2012)

Spectral Density

Two components

- Continuous distribution of modes with $\omega_k \leq k_B T$
- High energy quantised vibrations $\omega_k \gg k_B T$



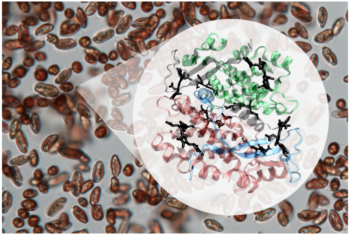


Image: E.J.O (Recharge magazine Feb 2012)

Quantum treatment of localised modes

System: Electronic dof and high energy resonant modes

$$H_S = H_{el} + H_{\text{modes}} + H_{el-\text{modes}}$$

$$H_{\text{modes}} = \sum_{m=1}^{2} \omega_{mode} B_m^\dagger B_m$$

$$H_{el-\text{modes}} = \sum_{m=1}^{2} g\sigma_m^+ \sigma_m^- \otimes \left(B_m^\dagger + B_m\right)$$

Bath: Continuous distribution of modes with cutoff frequency Ω_c

- $\omega_{mode} \gg k_B T, \Omega_c$
- perturbative theories not appropiate in general

Hierarchical equations of motion (HEOM)

The exact expression of Feynman-Vernon influence functional for Gaussian bath leads to a hierarchy of coupled equations of motion for the reduced density matrix of the system $\rho_S(t)$:

$$\partial_t \rho_S(t) = -i/\hbar[H_S(t), \rho_S(t)] + \int\int \mathcal{D}q\mathcal{D}q' e^{iS[q]/\hbar} \partial_t \mathcal{F}(q, q') e^{-iS[q']/\hbar} .$$

- $J(\omega) = 2\frac{\lambda\Omega_c}{\hbar}\frac{\omega}{\omega^2+\Omega_c{}^2}$
- $C_m(t) = \langle B_m(t) B_m(0)\rangle_B = \sum_k c_{mk} e^{-\nu_{mk} t}$

$$\begin{aligned}
\partial_t \rho_{\underline{\boldsymbol{n}}}(t) &= -i/\hbar[H_S, \rho_{\underline{\boldsymbol{n}}}(t)] + \cdots \\
&- \sum_m^N \sum_k n_{mk} v_{mk} \rho_{\underline{\boldsymbol{n}}} + \cdots \\
&- i \sum_m^N \left[\mathcal{V}_m, \sum_k \rho_{\underline{\boldsymbol{n}}^+_{mk}}\right] + \cdots \\
&- i \sum_m^N \sum_k n_{mk} \left(c_{mk} \mathcal{V}_m \rho_{\underline{\boldsymbol{n}}^-_{mk}} - c^*_{mk} \rho_{\underline{\boldsymbol{n}}^-_{mk}} \mathcal{V}_m\right) .
\end{aligned}$$

$\underline{\boldsymbol{n}} = \{\{\}, \cdots, \{n_{m1}, \cdots, n_{mk}\}, \cdots\}$, Tier $n = \sum_{mk} n_{mk}$

$$\ddots \quad \iddots \quad \ddots \quad \iddots \quad \ddots \quad \iddots \qquad \vdots$$

$$\rho_{\{2,0\}} \qquad \rho_{\{1,1\}} \qquad \rho_{\{0,2\}} \qquad\qquad \rho_{\underline{\mathbf{2}}}$$

$$\rho_{\{1,0\}} \qquad \rho_{\{0,1\}} \qquad\qquad \rho_{\underline{\mathbf{1}}}$$

$$\rho_{\{0,0\}} \qquad\qquad \rho_{\underline{\mathbf{0}}} = \rho_S$$

2 sites, $K_{trunc} = 0$

- Suitable for calculations at room temperature (T=300K)
- Exact if highest tier included $\mathcal{N} \gg \frac{\omega_e}{min(\nu_{mk})}$

Tanimura *et.al.* JPhysSocJapan 1989, Ishizaki *et.al.* JCP 2009

$\underline{\boldsymbol{n}} = \{\{\}, \cdots, \{n_{m1}, \cdots, n_{mk}\}, \cdots\},$ Tier $n = \sum_{mk} n_{mk}$

Results

Key questions:

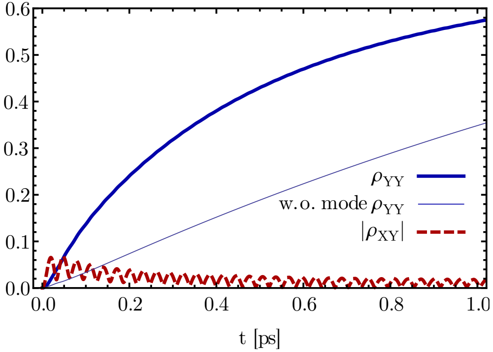
- Long lived electronic coherences
- Influence of high energy modes ($\omega_{mode} \gg k_B T$)

Result: Vibration-activated transport

Initial state:

$$\rho_S(0) = |X\rangle\langle X| \otimes \frac{e^{-\beta H_{\mathrm{modes}}}}{\mathrm{Tr}\{e^{-\beta H_{\mathrm{modes}}}\}} \qquad (1)$$

Truncate modes to maximum Fock level M.



Signatures of non-classicality

-Experiments: superpositions of vibrational states
-Quantify coherence in the Glauber sense
Mandel Q parameter:

$$Q = \frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle} - 1$$

Poissonian

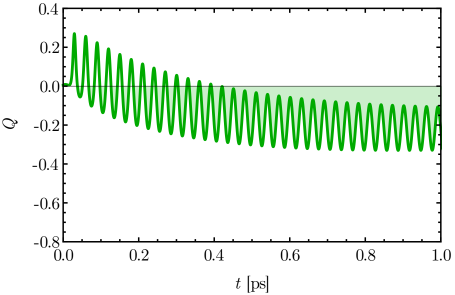
- $Q_{\text{coherent}} = 0$

Super-Poissonian

- $Q_{\text{thermal}} = (e^{\beta\omega_{\text{mode}}} - 1)^{-1}$
- $Q_{\text{displaced thermal}} > 0$

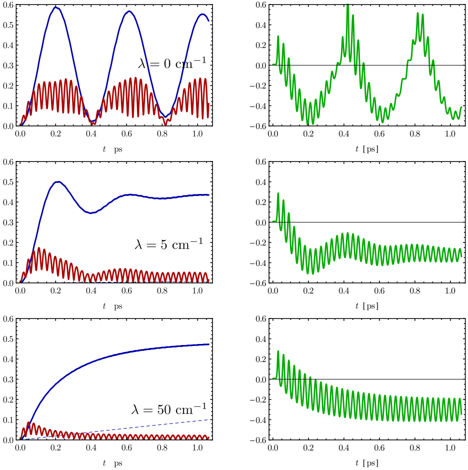
Sub-Poissonian ($Q > 0$)

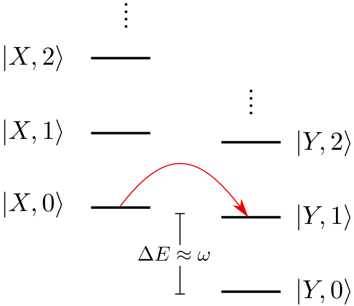
- $Q_{\text{Fock}} = -1$



Signatures of non-classicality

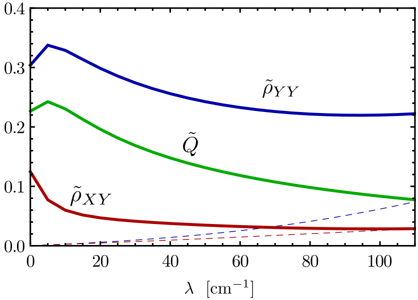
System Dynamics / Mandel Q





- Selective population of $|Y,1\rangle$

Result: Optimal Transport



Averages

$$\tilde{\rho}_{YY} = \frac{1}{\tau}\int_0^{\tau} \rho_{YY}(t)\mathrm{d}t$$

$$\tilde{\rho}_{XY} = \frac{1}{\tau}\int_0^{\tau} |\rho_{XY}(t)|\mathrm{d}t$$

$$\tilde{Q} = \frac{1}{\tau}\int_0^{\tau} -Q(t)\Theta[-Q(t)]\mathrm{d}t$$

Conclusions

- Noise: assists transport between energetically close states
- Quasi-resonant quantised vibrations: activate transfer between energetically distant states
- Optimal transport occurs for optimal non-classicality of mode (and non-zero electronic coherence)
- The combination of electronic and vibrational coherent contributions to dynamics can enhance performance
- Experimental methods to probe coherent contributions to dynamics