Hierarchy of Pure States applied to Photosynthetic Complexes

Daniel Süß

November 22nd, 2013

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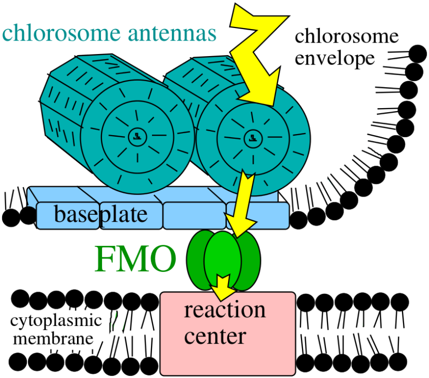
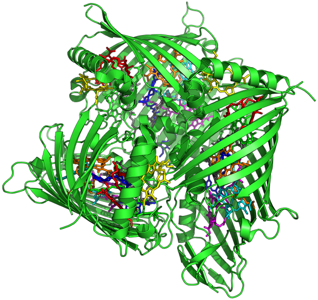
Light-Harvesting Complexes



- light absorbed at chlorosome antennas; transport to reaction center
- thermal noise in biological environment
- lifetime $\sim 2 - 5\,\mathrm{ps}$

http://www.pks.mpg.de/~eisfeld/wwww/images/green_bacteria_sketch.png

The Fenna-Matthews-Olson Complex



- found in green sulfur bacteria
- simplest pigment-protein complex
  - ideal test object
- quantum effects
- 3 identical, weakly coupled monomers + protein environment
- 8 Bacteriochlorophylls (BChls)
  - here: neglect BChl 8
- Energy received at BChls 1+6 transfered to sink at BChl 3

Tronrud et al., *Crystal structure of the Fenna-Matthews-Olson Protein from Chlorobaculum Tepidum*, 2009
Image created using Schrödinger, LLC, "The PyMOL Molecular Graphics System, Version 1.3r1", 2010

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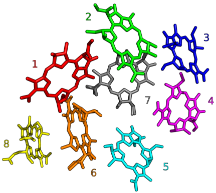

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Physical Model – Electronic System

- separation of electronic and vibrational degrees of freedom
  - electronic: valence electrons
  - vibrational: other electrons, nuclear DOF, environment
- one excited electronic state $|\pi_n\rangle$ per BChl *(exciton)*

$$H_{\mathrm{el}} = \sum_n \epsilon_n |\pi_n\rangle\langle\pi_n| + \sum_{m,n} V_{mn} |\pi_m\rangle\langle\pi_n|$$

(site energy ϵ_n; int. strength V_{mn})

- no effective transport $\Rightarrow$ influence of environment important

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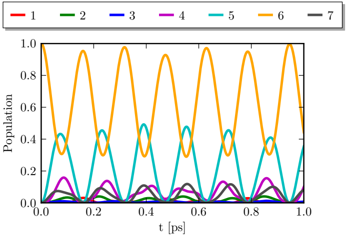
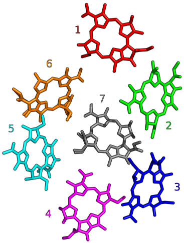


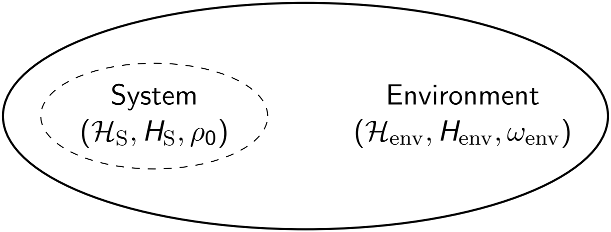


Open Quantum Systems

System
$(\mathcal{H}_{\mathrm{S}}, H_{\mathrm{S}}, \rho_0)$

Unknown time evolution

Open Quantum Systems



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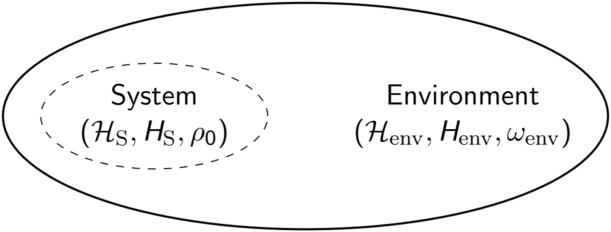
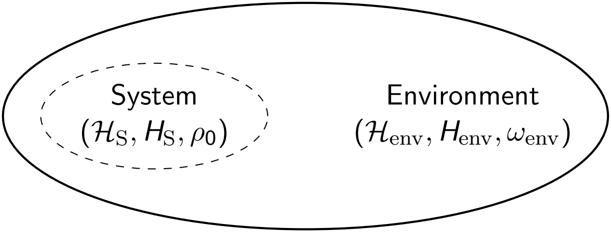


$$\mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{env}}$$

$$H_{\mathrm{S}} \otimes \mathrm{I} + \mathrm{I} \otimes H_{\mathrm{env}} + H_{\mathrm{int}}$$

$$\rho_0 \otimes \omega_{\mathrm{env}}$$

Open Quantum Systems



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$$H_{\mathrm{S}} \otimes \mathrm{I} + \mathrm{I} \otimes H_{\mathrm{env}} + H_{\mathrm{int}}$$
$$\rho_0 \otimes \omega_{\mathrm{env}}$$

$$\Longrightarrow \rho_t = \Lambda_t \rho_0 = \mathrm{Tr}_{\mathrm{env}} \left(U_t \rho \otimes \omega_{\mathrm{env}} U_t^\dagger \right)$$

$\rightarrow$ Common approach: Derive evolution equation for ρ_t.

Markovian Open Quantum Systems

Born-Markov approximation,
Completely positive time evolution

Linblad Master Equation *Quantum Trajectories*

Linblad Master Equation

$$\partial_t \rho_t = -\mathrm{i}[H, \rho_t] + \left([L\,\rho_t, L^\dagger] + [L, \rho_t\, L^\dagger]\right)$$

- "free", unitary time evolution + irreversible channel
- system of N^2 real valued ODEs

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Quantum Trajectories (diffusive, linear)

$$\mathrm{d}|\psi_t\rangle = \left(-\mathrm{i}H - \frac{1}{2}L^\dagger L\right)|\psi_t\rangle \mathrm{d}t + L|\psi_t\rangle\, \mathrm{d}\xi_t^*$$

- driven by complex white noise $\dot{\xi}_t$
- ρ_t recovered by "classical" average over independent realizations

$$\rho_t = \mathbb{E}\left(|\psi_t\rangle\langle\psi_t|\right) \approx \frac{1}{N}\sum_{n=1}^{N} |\psi_t^n\rangle\langle\psi_t^n|$$

- system of $2N$ real valued SDEs, trivial parallelization

$\rightarrow$ failure of Markovian theory due to strong coupling, "memory" in time evolution (or initial entanglement)

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Standard Open System Model

- specific model for environment: harmonic oscillators, linearly coupled

$$H_{\text{tot}} = H_{\text{sys}} + \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda + \sum_\lambda \left(g_\lambda^* L a_\lambda^\dagger + g_\lambda L^\dagger a_\lambda \right)$$

- interaction picture with respect to H_{env}

$$H_{\text{tot}}(t) = H_{\text{sys}} + \sum_\lambda \left(g_\lambda^* L a_\lambda^\dagger \, \mathrm{e}^{\mathrm{i}\omega_\lambda t} + g_\lambda L^\dagger a_\lambda \, \mathrm{e}^{-\mathrm{i}\omega_\lambda t} \right)$$

- Schrödinger equation for system and environment

$$\partial_t |\Psi_t\rangle = -\mathrm{i} H_{\text{tot}}(t) |\Psi_t\rangle, \qquad |\Psi_0\rangle = |\psi_0\rangle \otimes |0\rangle$$

- coherent state representation for bath DOF $\psi_t(\mathbf{z}^*) = \langle \mathbf{z} | \Psi_t \rangle$

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Non-Markovian Stochastic Schrödinger Equation

$$\partial_t \psi_t(\mathbf{z}^*) = -\mathrm{i}H_{\mathrm{sys}}\,\psi_t(\mathbf{z}^*) + L\,\boxed{Z_t^*}\,\psi_t(\mathbf{z}^*) - L^\dagger \int_0^t \boxed{\alpha(t-s)}\,\frac{\delta\psi_t(\mathbf{z}^*)}{\delta Z_s^*}\,\mathrm{d}s$$

- "stochastic process" $Z_t^* = -\mathrm{i}\sum_\lambda g_\lambda^* z_\lambda^* \mathrm{e}^{\mathrm{i}\omega_\lambda t}$
- bath correlation function $\alpha(t) = \sum_\lambda |g_\lambda|^2\,\mathrm{e}^{-\mathrm{i}\omega_\lambda t}$

- only dependence on z_λ^* through $Z_t^* \Rightarrow \psi_t(\mathbf{z}^*) \to \psi_t(Z^*)$
- stochastic Schrödinger equation for quantum trajectories $\psi_t(Z^*)$ with

$$\mathbb{E}Z_t = 0, \quad \mathbb{E}(Z_t Z_s) = 0, \quad \text{and} \quad \mathbb{E}(Z_t Z_s^*) = \alpha(t-s)$$

$$\rho_t = \mathrm{Tr}_{\mathrm{env}}|\Psi_t\rangle\langle\Psi_t| = \mathbb{E}\left(|\psi_t(Z^*)\rangle\langle\psi_t(Z^*)|\right)$$

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- "stochastic process" $\quad Z_t^*$
- bath correlation function $\alpha(t) = \int_0^\infty J(\omega) \mathrm{e}^{-\mathrm{i}\omega t}\, \mathrm{d}\omega$

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Diósi, Gisin, and Strunz, "Non-Markovian quantum state diffusion", 1998

Hierarchy of Pure States (HOPS)

$$\partial_t\psi_t = -\mathrm{i}H_{\mathrm{sys}}\psi_t + LZ_t^*\psi_t - L^\dagger \underbrace{\int_0^t \alpha(t-s)\frac{\delta\psi_t}{\delta Z_s^*}\,\mathrm{d}s}_{=:\psi_t^{(1)}}$$

- closed time evolution equation in case $\alpha(t) = g\,\mathrm{e}^{-\gamma|t|-\mathrm{i}\Omega t}$

$$\begin{aligned}
\partial\psi_t^{(0)} &= \left(-\mathrm{i}H_{\mathrm{sys}} + LZ_t^*\right)\psi_t^{(0)} && && - L^\dagger\psi_t^{(1)} \\
\partial\psi_t^{(1)} &= \left(-\mathrm{i}H_{\mathrm{sys}} - (\gamma+\mathrm{i}\Omega) + LZ_t^*\right)\psi_t^{(1)} && +g\;L\psi_t^{(0)} && - L^\dagger\psi_t^{(2)} \\
&\;\;\vdots \\
\partial\psi_t^{(k)} &= \left(-\mathrm{i}H_{\mathrm{sys}} - k(\gamma+\mathrm{i}\Omega) + LZ_t^*\right)\psi_t^{(k)} && +kg\;L\psi_t^{(k-1)} && - L^\dagger\psi_t^{(k+1)} \\
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Truncation of the Hierarchy

$$\partial_t \psi_t^{(k)} = \left(-\mathrm{i}H_{\mathrm{sys}} - k(\gamma + \mathrm{i}\Omega) + LZ_t^*\right)\psi_t^{(k)} + kg\, L\psi_t^{(k-1)} - L^\dagger \psi_t^{(k+1)}$$

$$\Updownarrow$$

$$\psi_t^{(k)} = \int_0^t \mathrm{e}^{-k(\gamma+\mathrm{i}\Omega)(t-s)} \ldots \left(kg\, L\psi_s^{(k-1)} - L^\dagger \psi_s^{(k+1)}\right) \mathrm{d}s$$

- truncation at finite order D with *terminator* (here: $\Omega = 0$)

$$\partial_t \psi_t^{(D)} = \left(-\mathrm{i}H_{\mathrm{sys}} - D\gamma + LZ_t^* - \frac{g}{\gamma} L^\dagger L\right)\psi_t^{(D)} + Dg\, L\psi_t^{(D-1)}$$

- "Markovian" approximation for D^{th} order

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Further Remarks

- no simple criterion to determine D $\rightarrow$ individual checking necessary
- rule of thumb: large truncation order D for
  - small memory time $\iff$ large γ
  - strong coupling $\iff$ large g
- nonlinear version $\rightarrow$ proper importance sampling
- exponential BCF requires negative frequencies $\rightarrow$ unphysical

- proper treatment for $T \neq 0$

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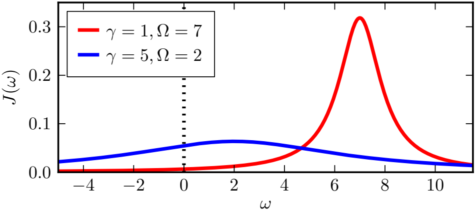

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The FMO-Complex – Full Model

- environment: independent, identical harmonic baths for each BChl
- all thermal effects included in *thermal correlation function*

$$\alpha(t) = \int_0^\infty J(\omega) \left(\coth\left(\frac{\omega}{2T}\right)\cos(\omega t) - \mathrm{i}\sin(\omega t)\right) \mathrm{d}\omega$$

- highly structured realistic spectral density
  - large number of exponential modes required
  - simplified spectral density (for $D = 2$: 120 vs. 15576 auxiliary states)

Wendling et al., "Electron—Vibrational Coupling in the Fenna—Matthews—Olson Complex of Prosthecochloris aestuarii Determined by Temperature-Dependent Absorption and Fluorescence Line-Narrowing Measurements", 2000

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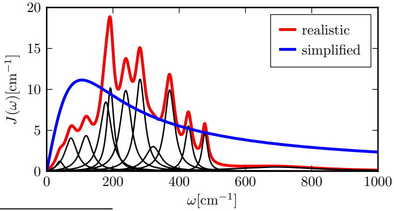

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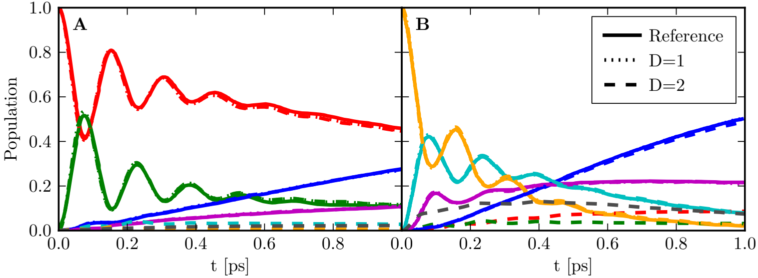
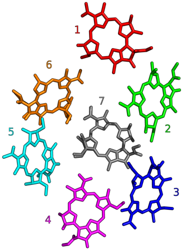
Exciton Transfer at Cryogenic Temperature





- directed energy transfer toward BChls 3 + 4
- yield of 40 % (resp. 75 %) on relevant BChls
- coherent, wavelike dynamics up to $t \approx 0.7\,\mathrm{ps}$

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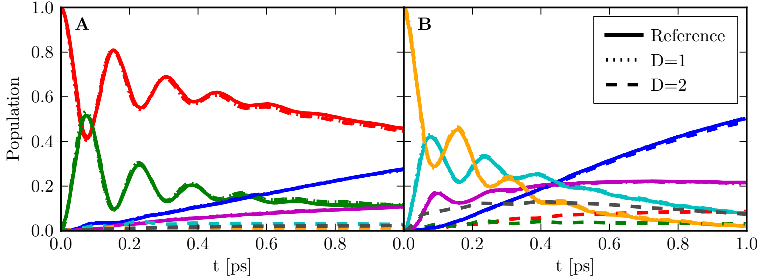

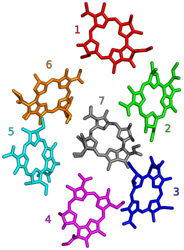

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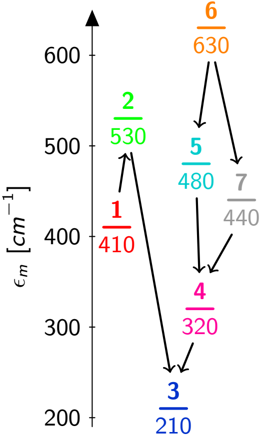

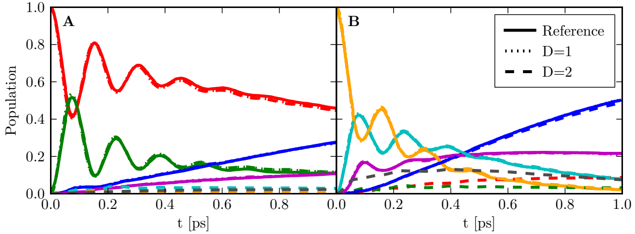

- two distinct transport channels
- potential step between BChls 1 & 2
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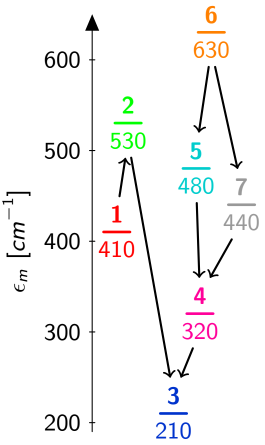
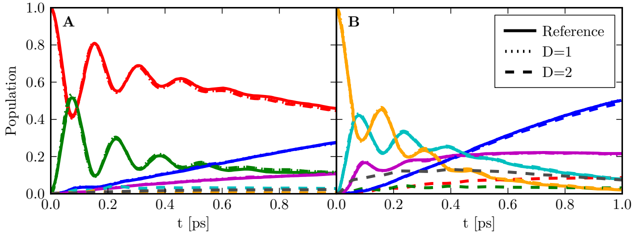
Exciton Transfer at Cryogenic Temperature





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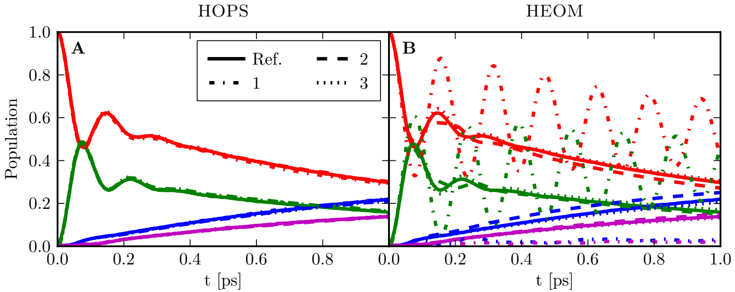

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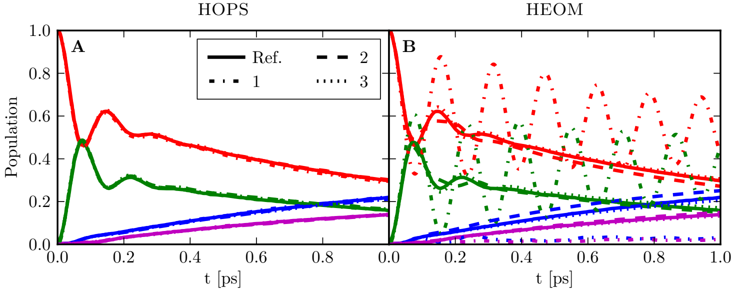

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