Theoretical Aspects of Quantum Effects in Biology

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&

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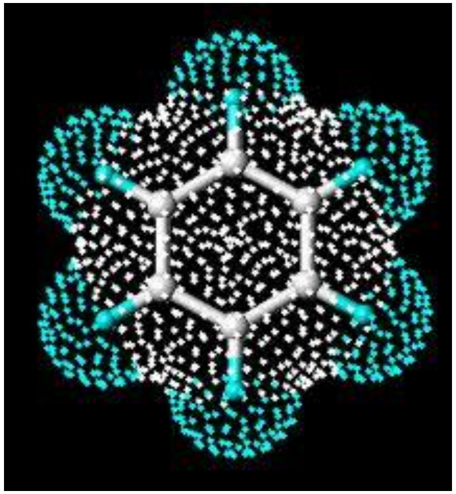
What we are looking for

- Quantum coherence certainly exists at the level of chemical bonds

  Electrons are delocalized in a coherent superposition

  For us this kind of coherence is of little relevance !

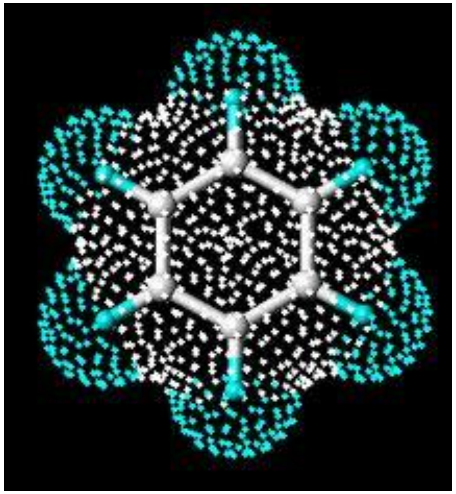
  Its in equilibrium , static, short-ranged



- More interesting is (transport) dynamics because
  - You learn about systems by poking them.
  - Biological processes are necessarily dynamic.
  - Has the potential to explore long range correlations.

What we are looking for

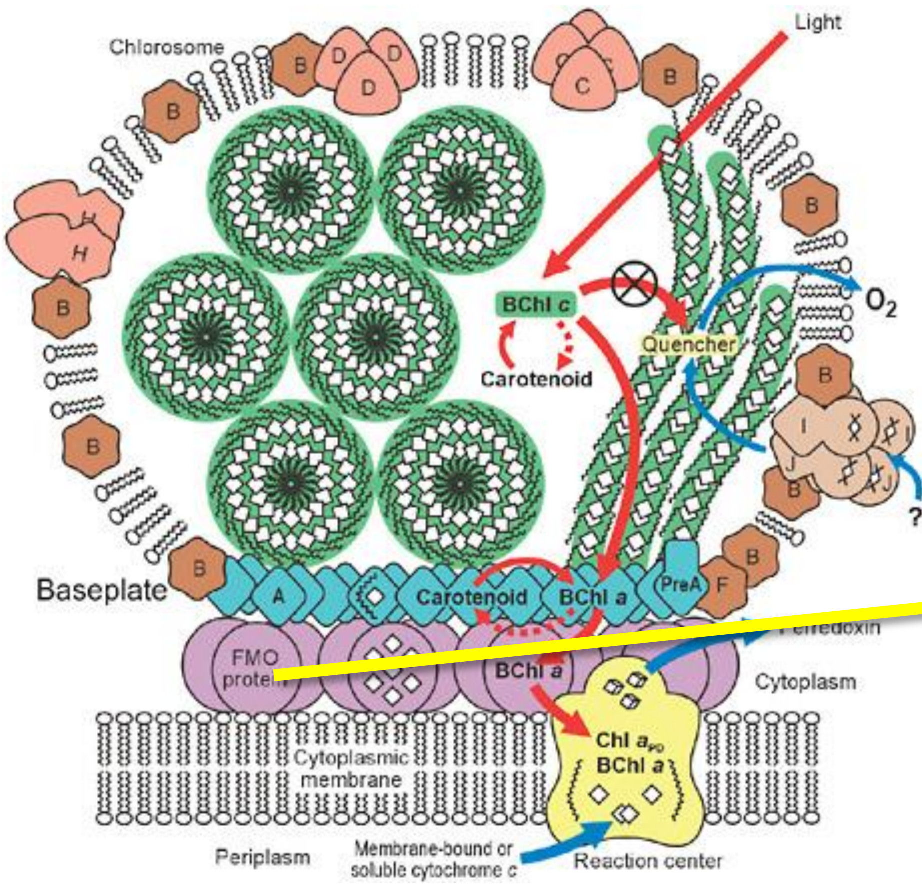
- Questions:



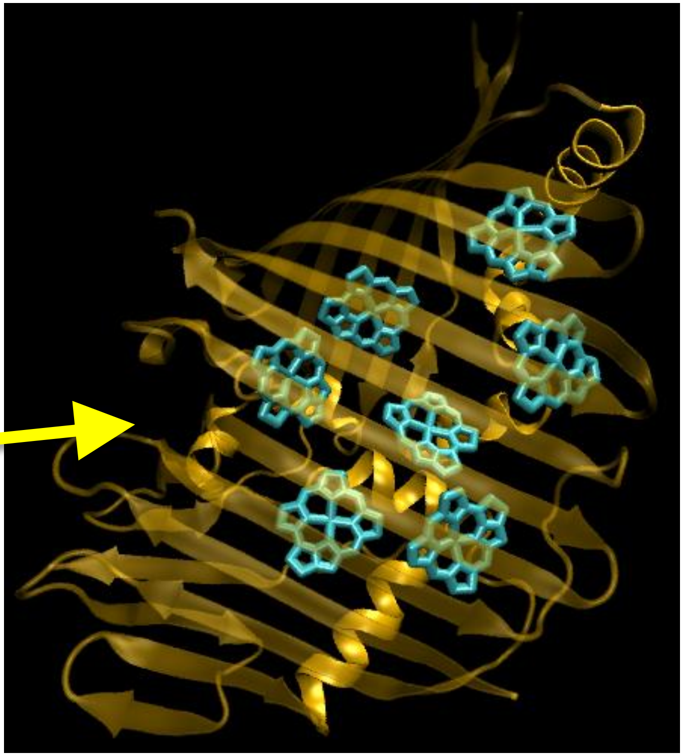
  - On what length and time scales do we find coherence ?
  - What, if any, is the role of coherence ?
  - What, if any, is the role of the environment ?
  - Can one quantify coherence and quantum character ?
  - How do I verify theoretical hypotheses experimentally ?

Excitation Transport in Noisy Environments

Photosynthetic Apparatus

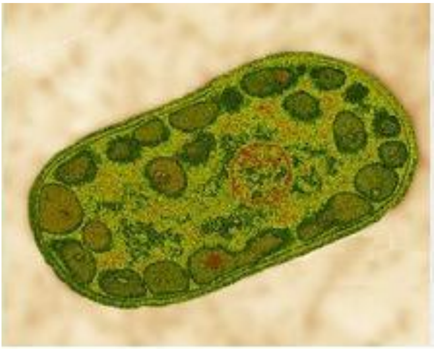


Fenna-Matthews-Olsen Complex (FMO)

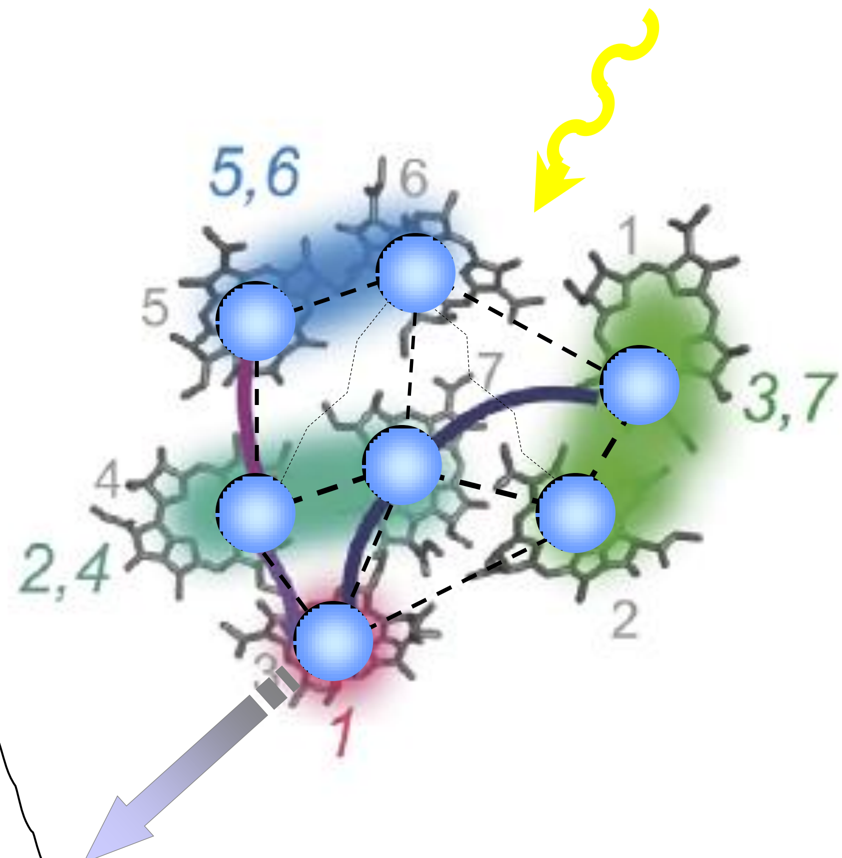


Lossless transport ~ 5 ps

Exciton Transport in Photosynthesis



Green sulphur Bacteria



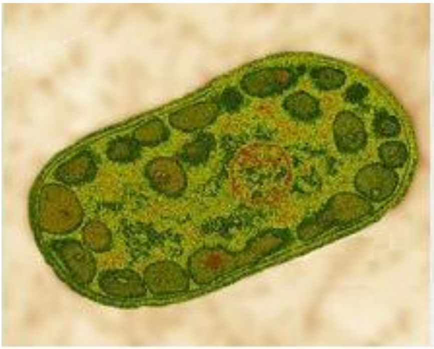
Reaction Centre

$CO_2 + 2\ H_2S$

+ energy

$CH_2O + 2\ S +\ H_2O$

Excitation Transport



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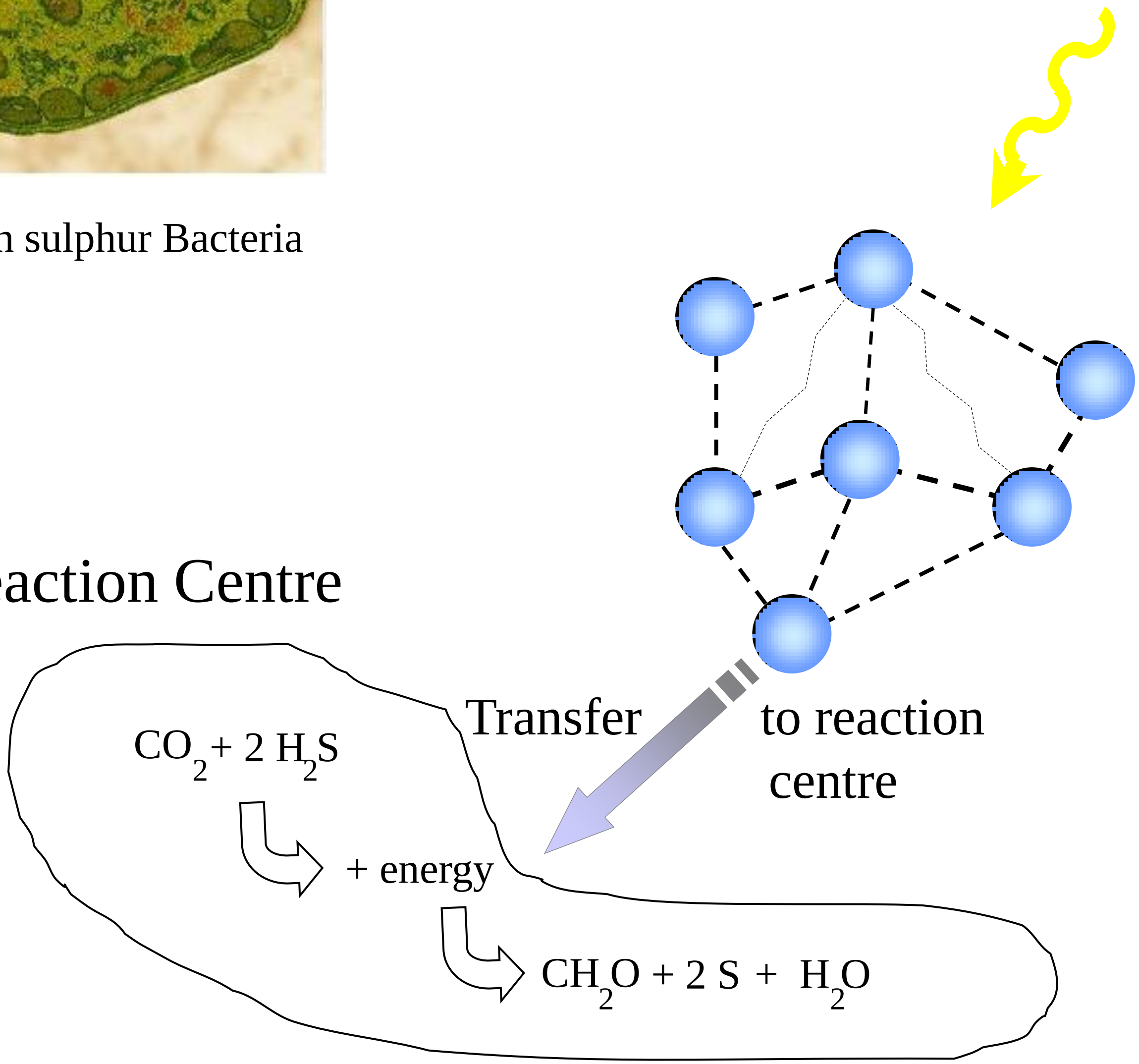
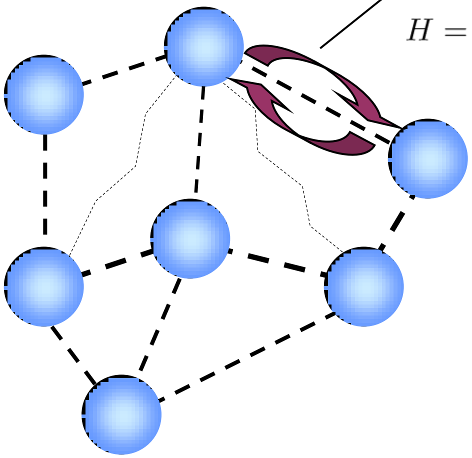


$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \mathcal{L}$$

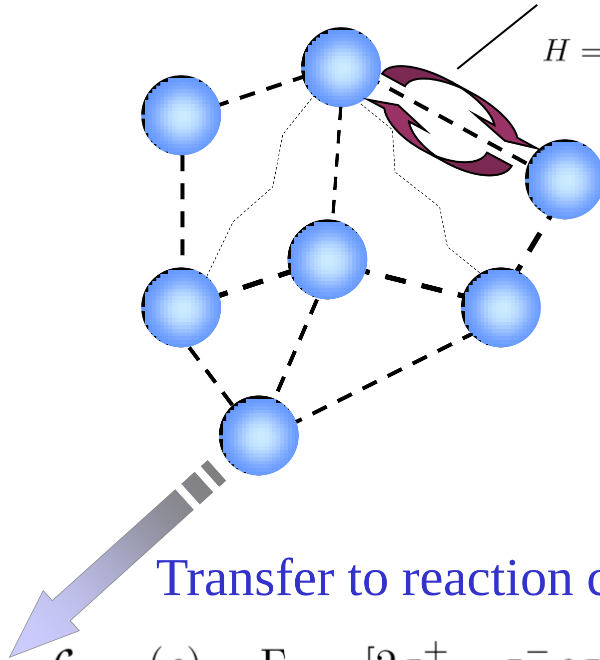


$$H = \sum_{j=1}^{N} \hbar\omega_j \sigma_j^+ \sigma_j^- + \sum_{j \neq l} \hbar v_{j,l} (\sigma_j^- \sigma_l^+ + \sigma_j^+ \sigma_l^-)$$

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \mathcal{L}$$

Exchange of excitation

$$H = \sum_{j=1}^{N} \hbar\omega_j \sigma_j^+ \sigma_j^- + \sum_{j \neq l} \hbar v_{j,l} (\sigma_j^- \sigma_l^+ + \sigma_j^+ \sigma_l^-)$$



Transfer to reaction centre

$$\mathcal{L}_{sink}(\rho) = \Gamma_{N+1}[2\sigma_{N+1}^+ \sigma_k^- \rho \sigma_k^+ \sigma_{N+1}^- - \{\sigma_k^+ \sigma_{N+1}^- \sigma_{N+1}^+ \sigma_k^-, \rho\}]$$

$$\mathcal{L}_{diss}(\rho) = \sum_{j=1}^{N} \Gamma_j [-\{\sigma_j^+ \sigma_j^-, \rho\} + 2\sigma_j^- \rho \sigma_j^+]$$

Loss of excitation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \mathcal{L}$$

Exchange of excitation

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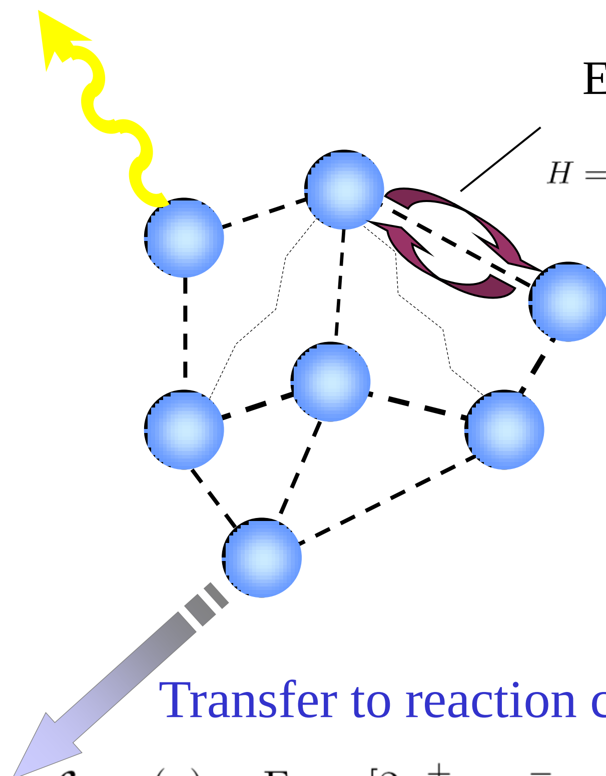

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$$\mathcal{L}_{diss}(\rho) = \sum_{j=1}^{N} \Gamma_j [-\{\sigma_j^+ \sigma_j^-, \rho\} + 2\sigma_j^- \rho \sigma_j^+]$$

Dephasing

Loss of excitation

Exchange of excitation

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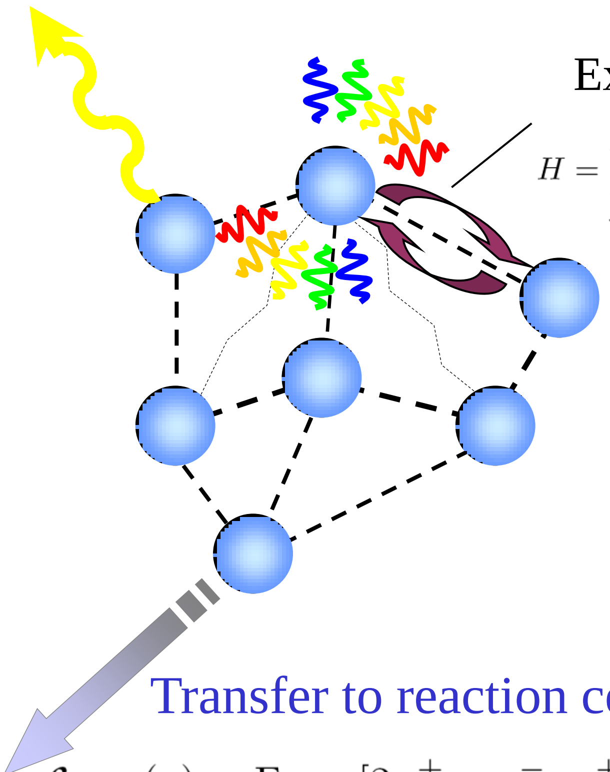

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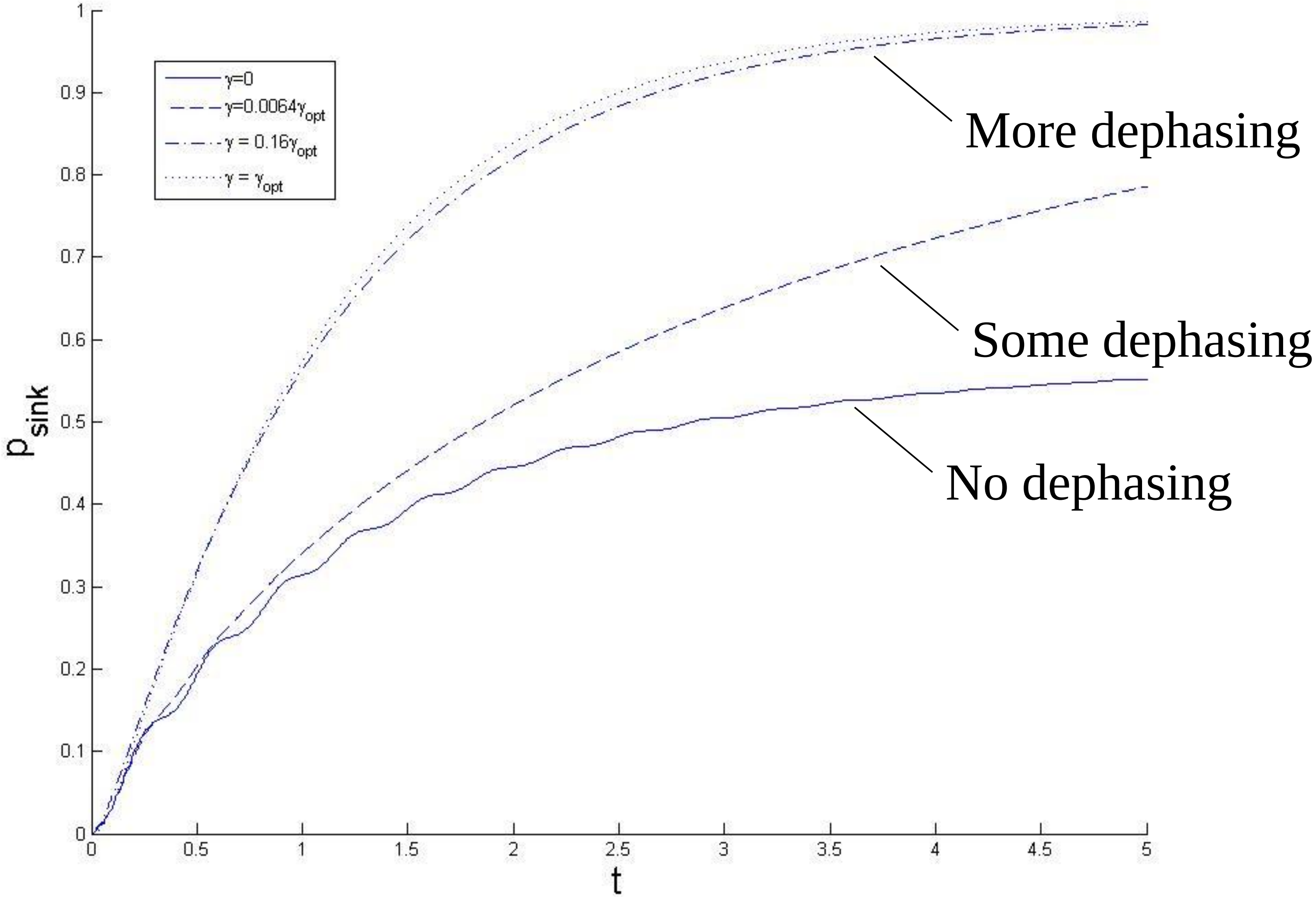
Noise Assisted Transport



Plenio & Huelga, New J. Phys. 2008
Caruso, Chin, Datta, Huelga, Plenio, J. Chem. Phys. 2009

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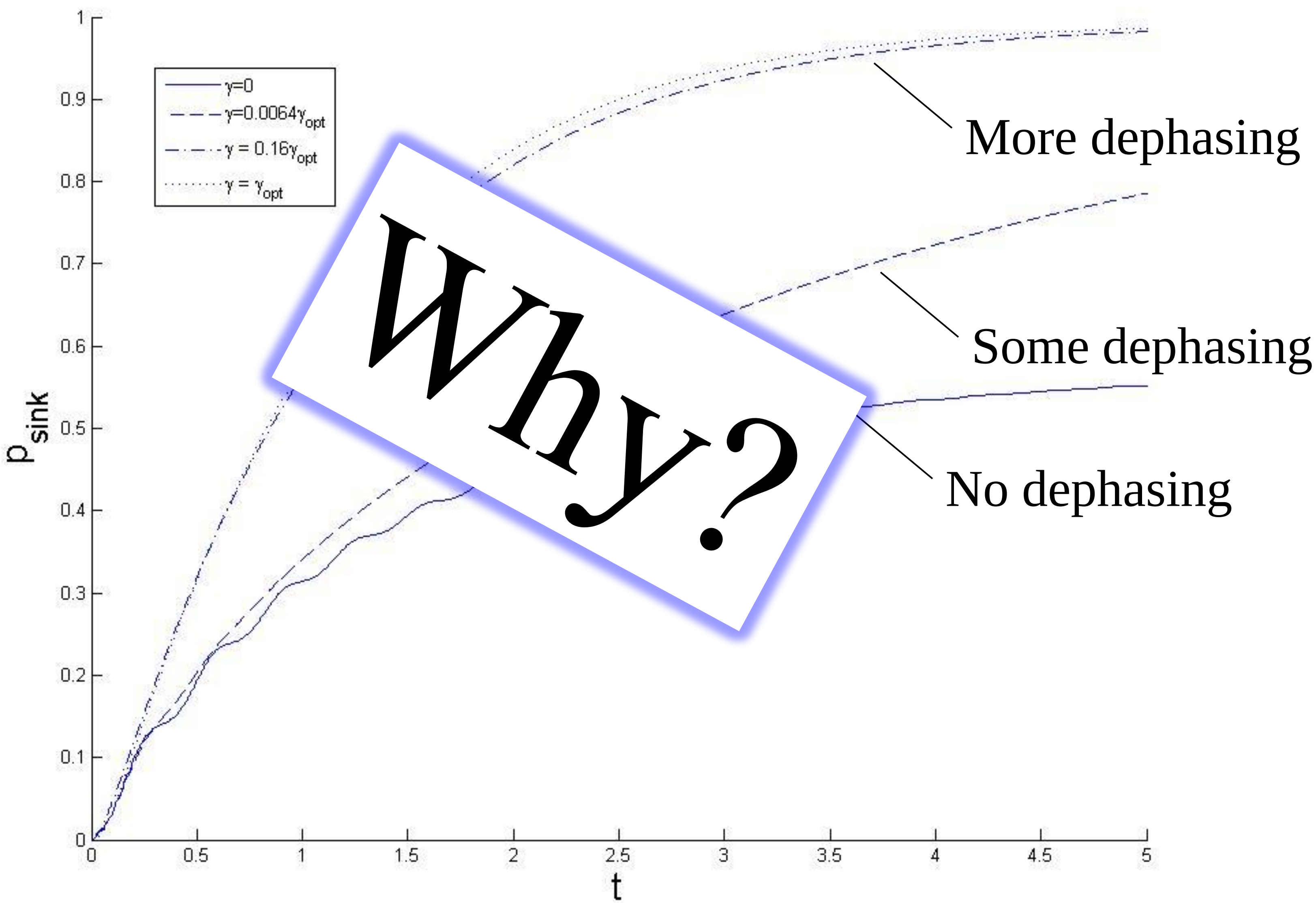

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Deconstruct the FMO Hamiltonian

Excitonic states that are excited have small overlap with sink.

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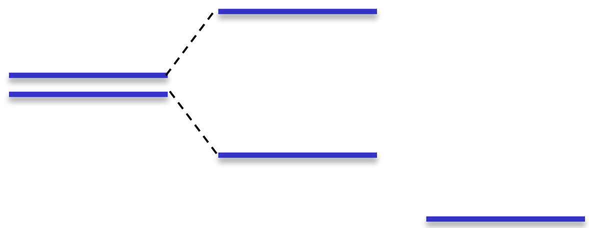
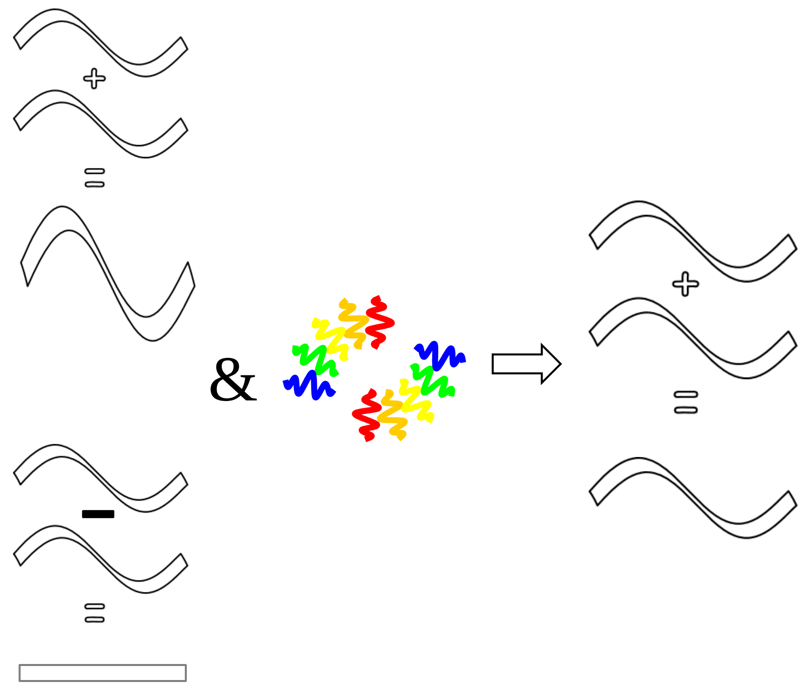
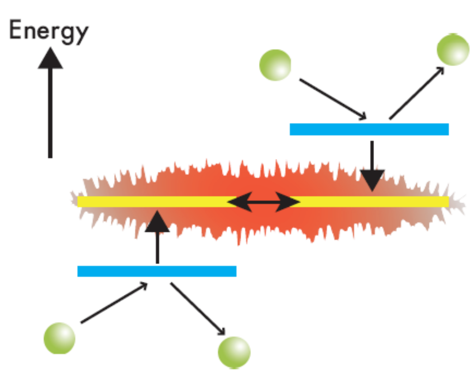
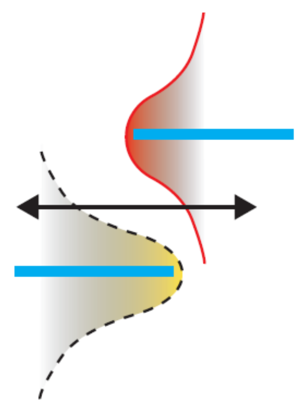
$$H=\begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix}$$

Deconstructing Coherence and Decoherence



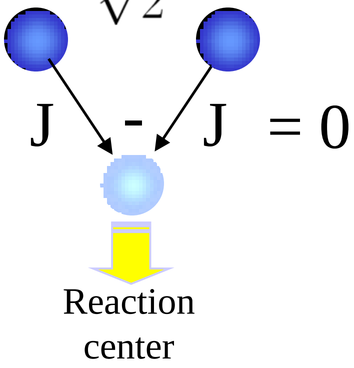






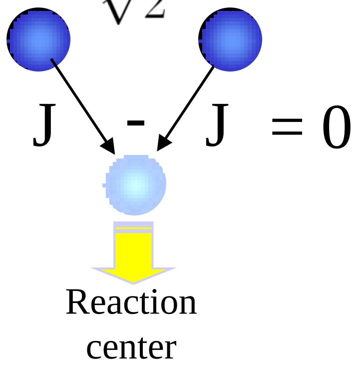
Destructive Interference and Invariant States

$$\frac{|10\rangle - |01\rangle}{\sqrt{2}} = |\Psi^{-}\rangle$$



Destructive Interference and Invariant States

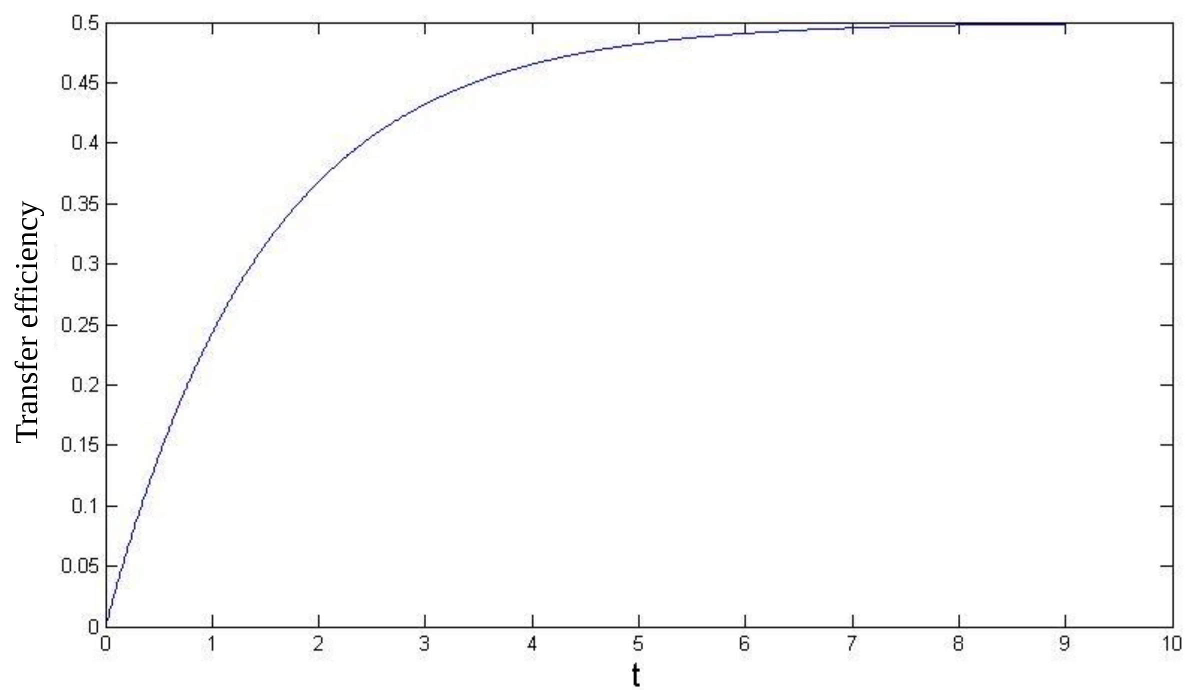
$$\frac{|10\rangle - |01\rangle}{\sqrt{2}} = |\Psi^-\rangle$$



$$|01\rangle = \frac{1}{\sqrt{2}}\left[\frac{|01\rangle - |10\rangle}{\sqrt{2}} + \frac{|01\rangle + |10\rangle}{\sqrt{2}}\right]$$

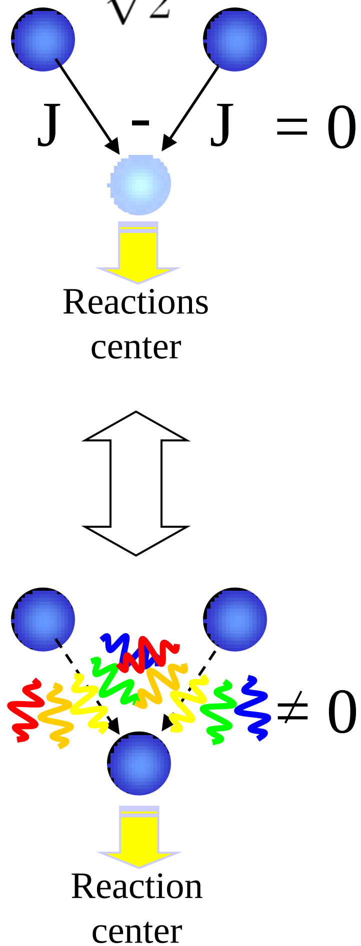
$$\Downarrow$$

$$\rho = \frac{1}{2}|\psi^-\rangle\langle\psi^-| + \frac{1}{2}|00\rangle\langle 00|$$



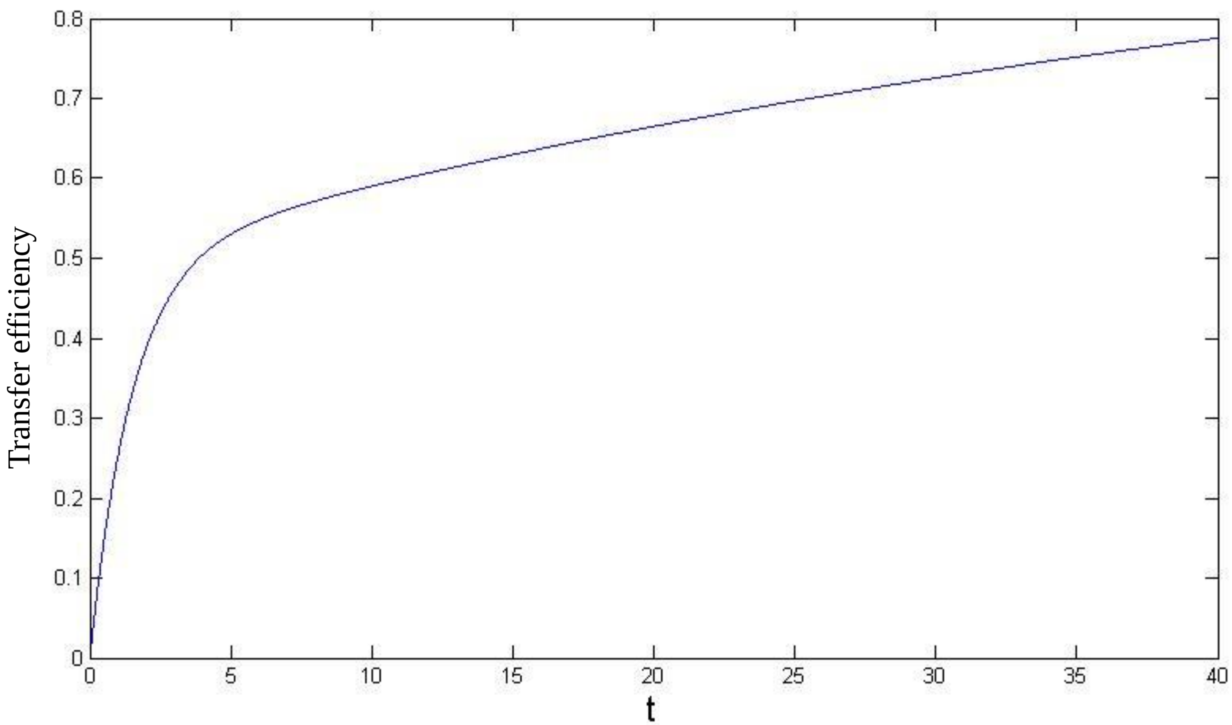
Noise Inhibits Destructive Interference

$$\frac{|10\rangle - |01\rangle}{\sqrt{2}} = |\Psi^-\rangle$$



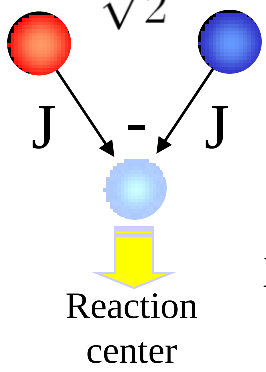
Reduction of destructive interference

Decoherence inhibits destructive interference !



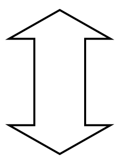
Disorder Inhibits Destructive Interference

$$\frac{|10\rangle - |01\rangle}{\sqrt{2}}$$

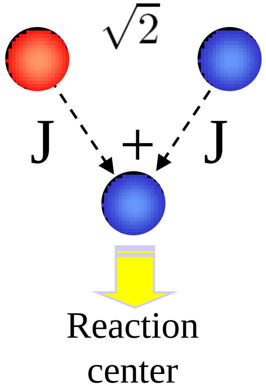


$= 0$

Destructive interference



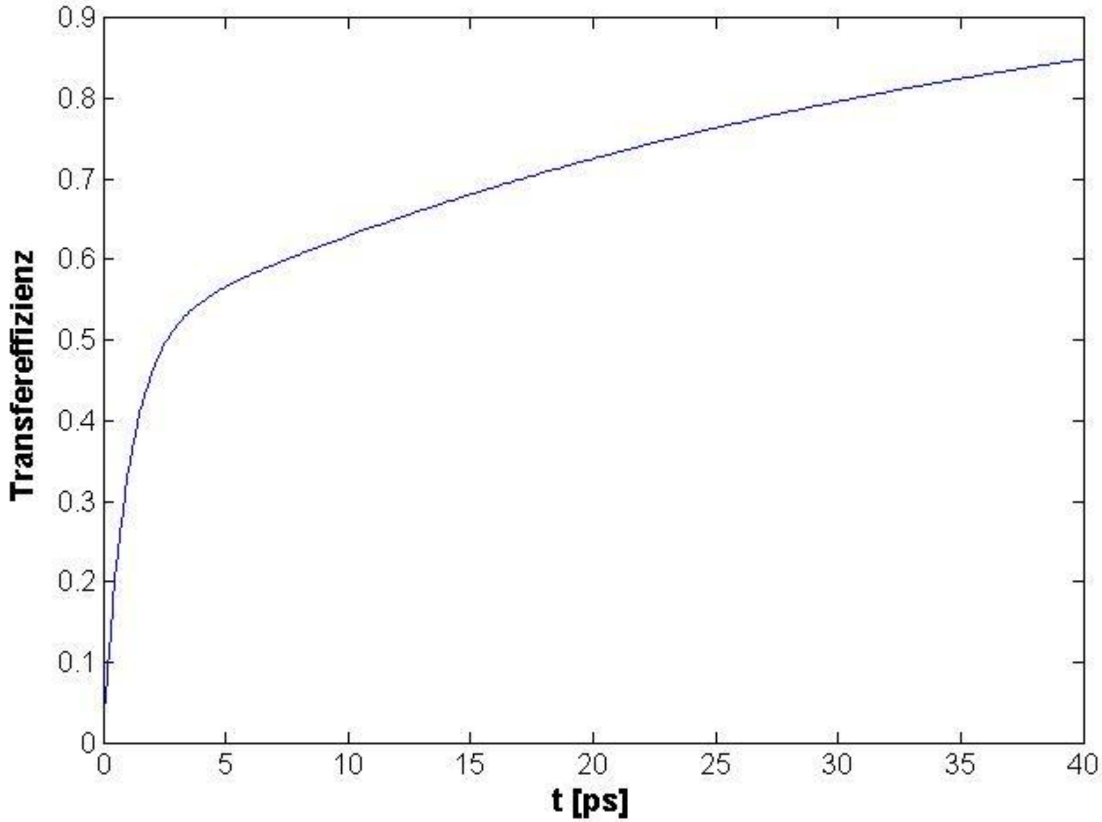
$$\frac{|10\rangle - e^{i\Delta\omega\, t}|01\rangle}{\sqrt{2}}$$



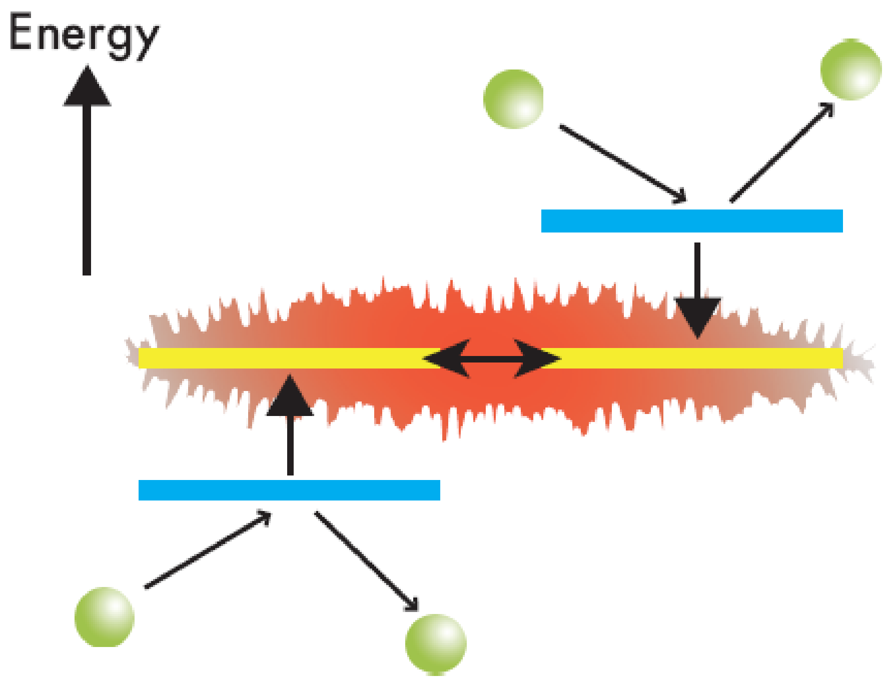
$\neq 0$

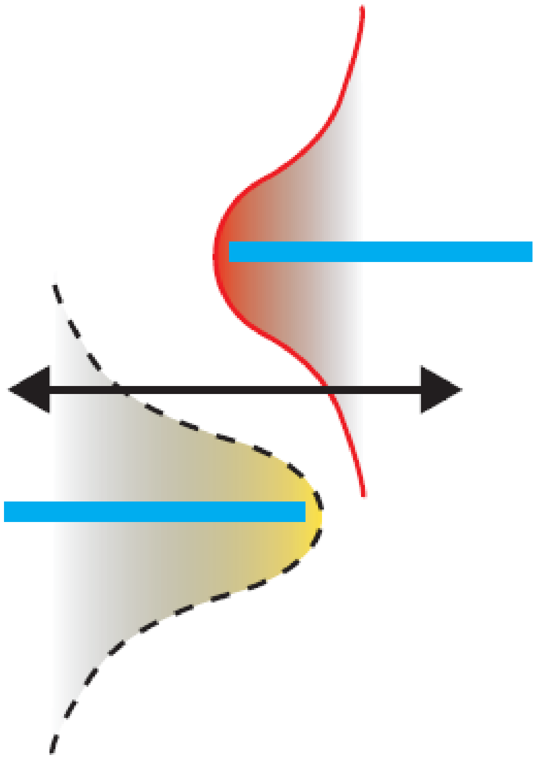
Reduction of destructive interference

Static disorder inhibits destructive interference !

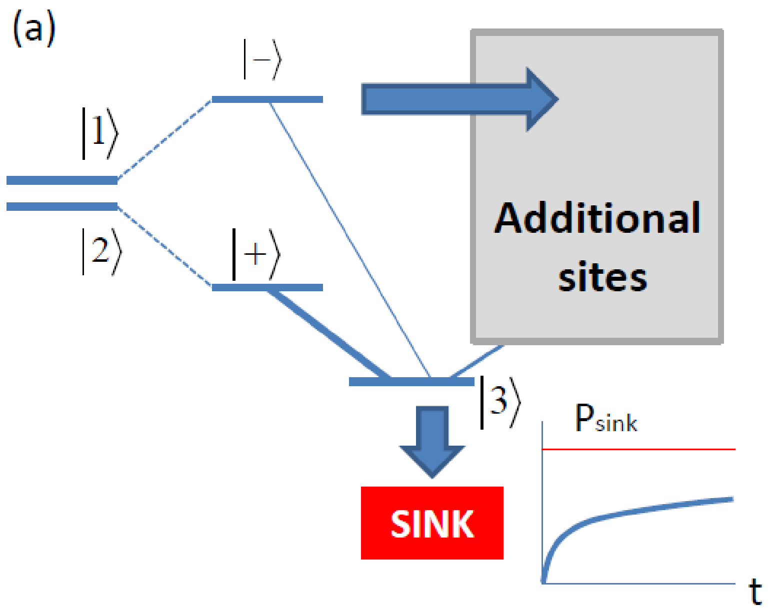


Noise bridges energy gaps





Coherence shifts resonances



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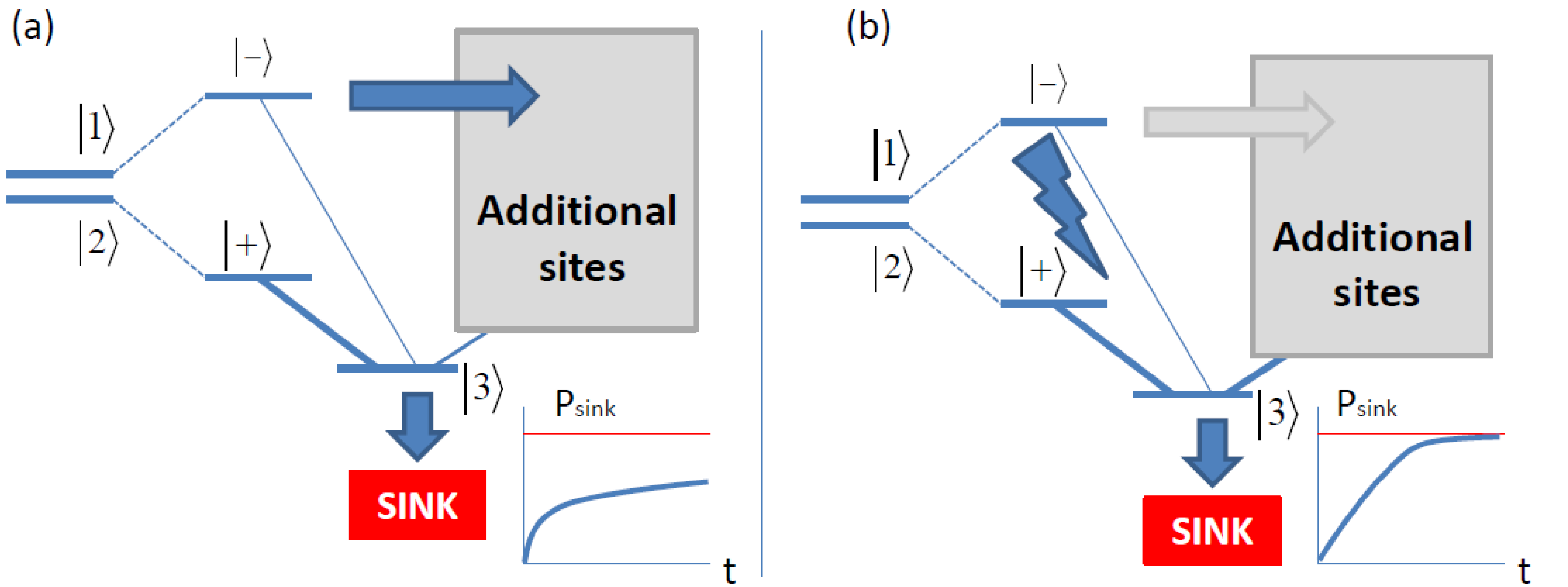

Caruso, Chin, Datta, Huelga, Plenio, J Chem Phys 2009
Chin, Caruso, Datta, Huelga, Plenio, NJP 2010

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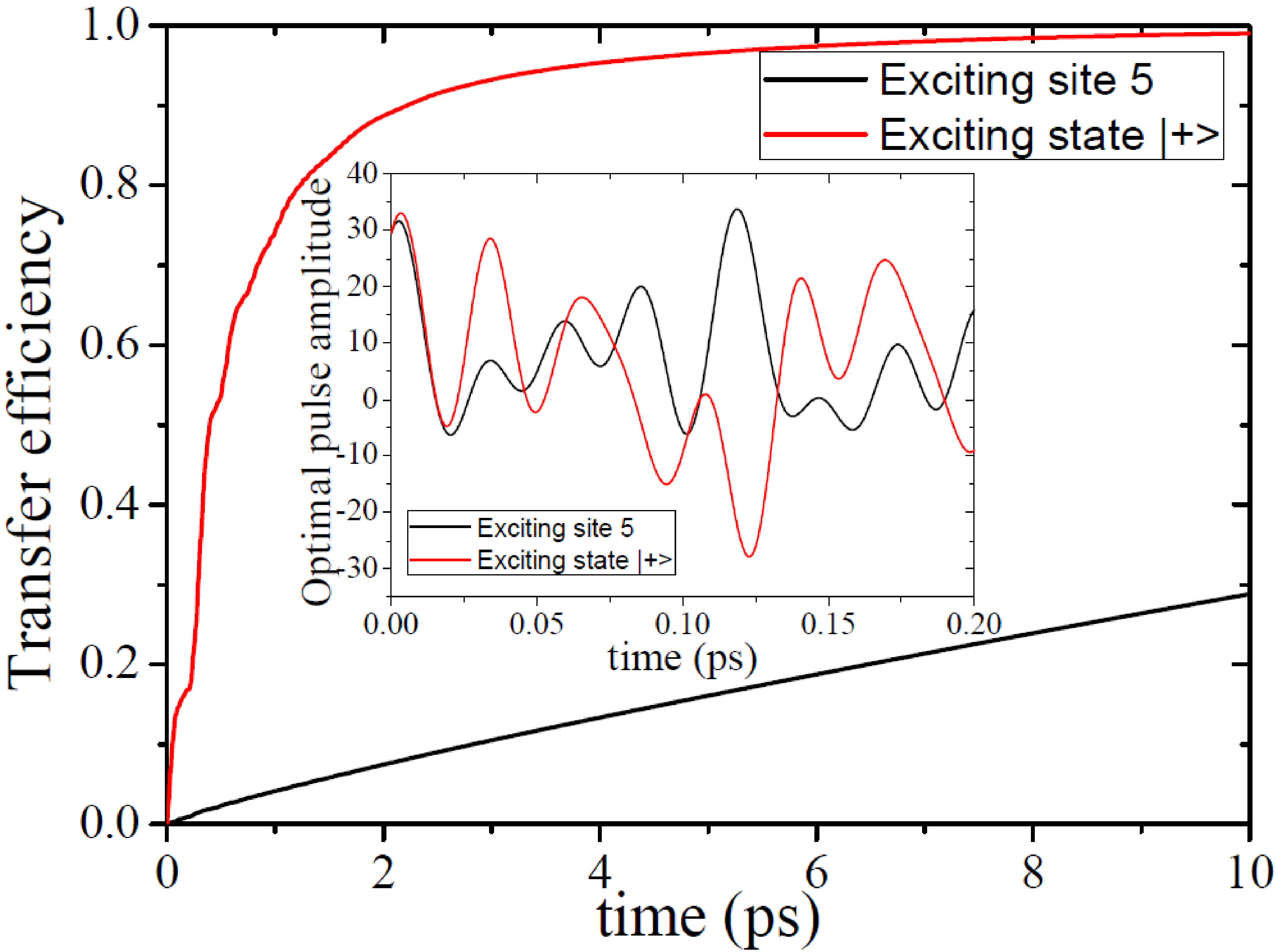
where we have shifted the zero of energy by 12 230 (all numbers are given in the units of $1.988\,865 \times 10^{-23}$ nm $= 1.2414 \times 10^{-4}$ eV) for all sites corresponding to a wavelength of $\cong$800 nm.

Can test the relevance of structural elements for dynamics by selectively adding noise in computer simulation, but ...

... test in real system would be more convincing

Use optimal control for experimental tests



Caruso, Montangero, Calarco, Huelga, Plenio, in preparation

System – Environment Description

Need description of the dynamics of complex quantum systems in the presence of intermediate noise levels

- Master equation approaches (perturbative)
  not accurate as interaction is comparable to intersite interaction

- Nakajima-Zwanzig (time non-local)
  in principle exact but impossible to solve

- Hierarchy methods
  hard for arbitrary spectral densities

Ishizaka & Fleming, J. Chem. Phys. 2009
Ishizaki et al, Phys Chem Chem Phys 2010

- Transformation techniques
  Efficient but correlated noise may be challenging

Prior, Chin, Huelga, Plenio, PRL 2010
Chin, Rivas, Huelga, Plenio, J Math Phys 2010

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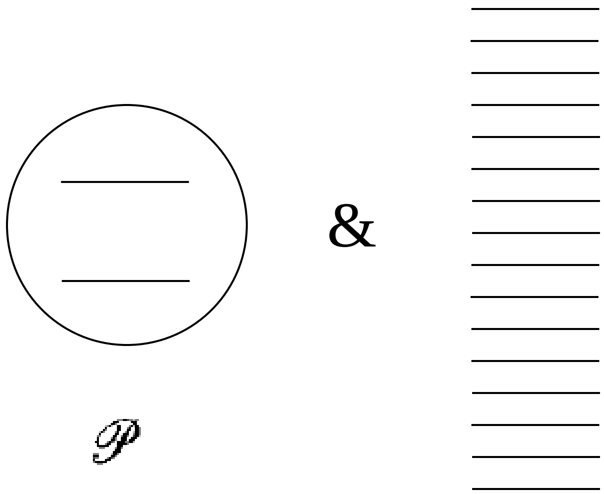

Evolution equation of global system

$$\dot{\rho} = L\rho$$

We are interested in dynamics of the system only $\Rightarrow \mathscr{P}\rho$

$$\frac{d}{dt}\mathscr{P}\rho = \mathscr{P}L\mathscr{P}\rho + \mathscr{P}L(1-\mathscr{P})\rho$$

$$\frac{d}{dt}(1-\mathscr{P})\rho = (1-\mathscr{P})L(1-\mathscr{P})\rho + (1-\mathscr{P})L\mathscr{P}\rho$$

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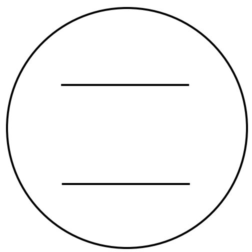

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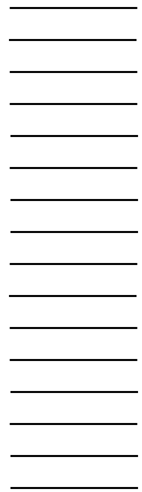

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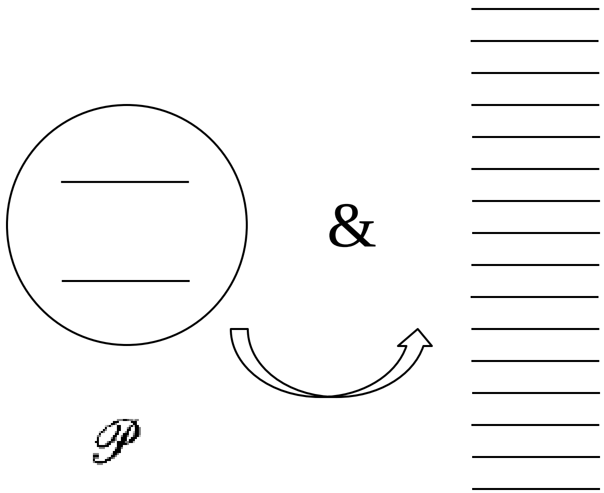

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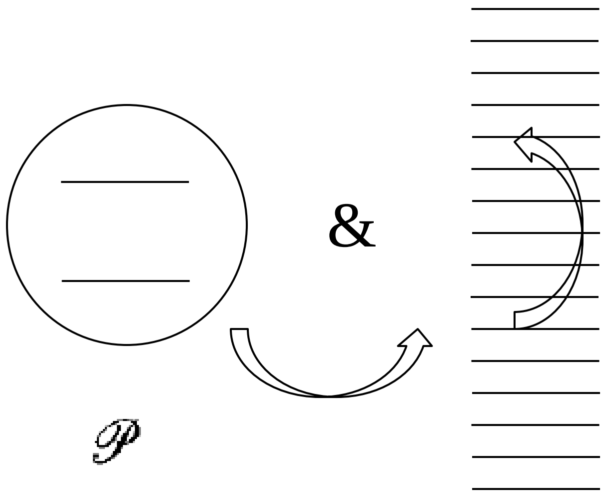

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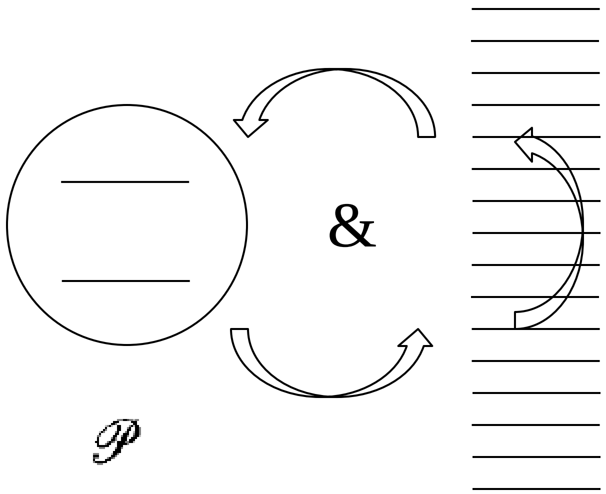

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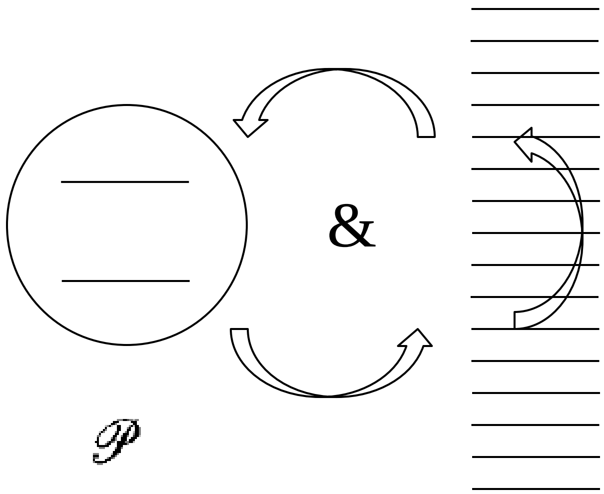

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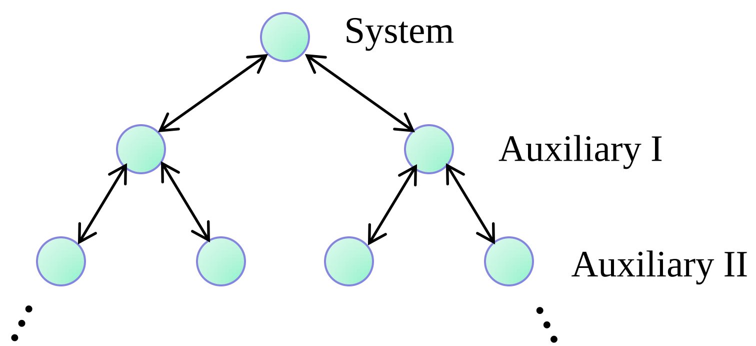
perturbative $\Leftarrow$ Gives Lindblad/Redfield $\rho(t)$

System – Environment Description

Hierarchy method aims to replace integral solution by a set of coupled differential equations with auxiliary operators.

- Has been applied successfully for specific spectral densities (FMO ..)
- Number of elements in hierarchy can grow rapidly
- Coefficients can be hard to compute for general spectral densities
- Error in cut-off not known

Ishizaka & Fleming, J. Chem. Phys. 2009
Ishizaki et al, Phys Chem Chem Phys 2010

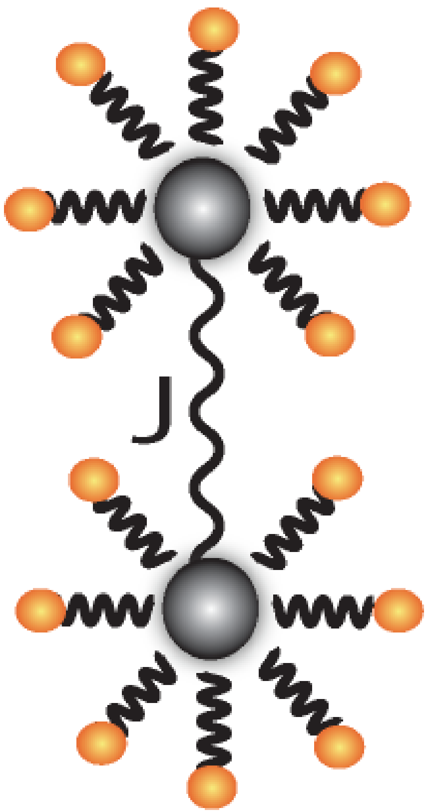


Would like method with controllable and certifiable error that keeps all available information.

Transforming the spin-boson model

Aim: Full many-body simulation, treat system and bath on equal footing for arbitrary bath spectral densities

Method of choice for 1-D systems: T-DMRG – Numerically exact method for highly-correlated many-body systems in 1D



Problem: Geometry of spin-boson model is not T-DMRG friendly

Transforming the spin-boson model

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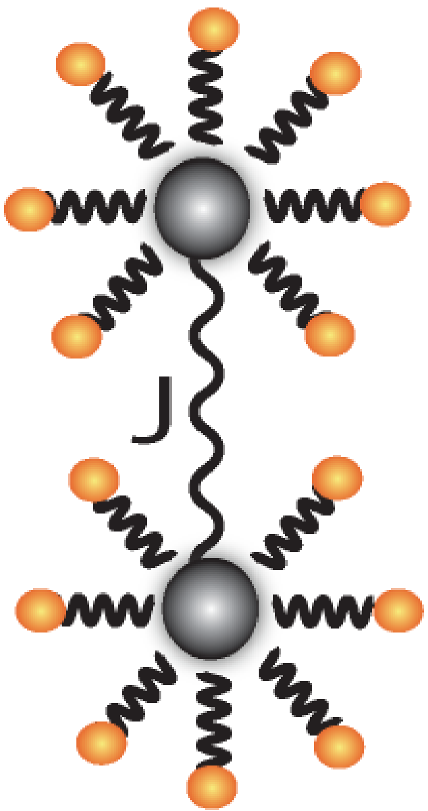
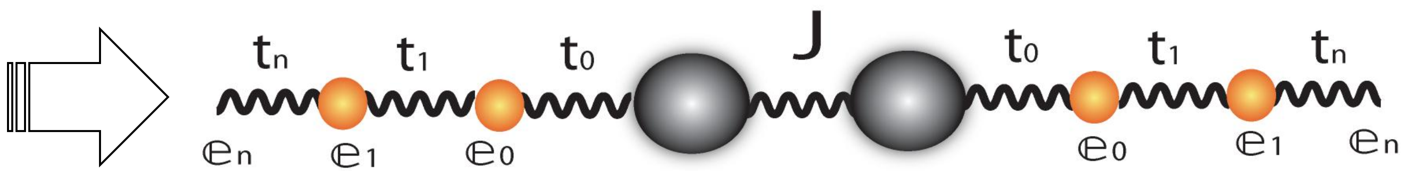




Previous implementations – discrete, numerically unstable. Bulla, Tong & Vojta, Phys. Rev. Lett. 2003; Bulla, Lee, Tong, & Vojta, Phys. Rev. B 2005.

New – Analytical mapping with orthogonal polynomials

Prior, Chin, Huelga, Plenio, PRL 2010
Chin, Rivas, Huelga, Plenio, J Math Phys 2010

Alternative via (discrete) orthogonal polynomials

$$H_{\rm res} = \int_0^{x_{\max}} dx g(x) a_x^\dagger a_x$$

usually

$$g(x) = gx$$

$$V = \int_0^{x_{\max}} dx h(x) \hat{A}(a_x + a_x^\dagger)$$

Goal: Find new modes

$$b_n^\dagger = \int_0^{x_{\max}} dx\, U_n(x) a_x^\dagger$$

Each $U_n(x)$ can be considered a (orthonormal) polynomial !

such that

$$c_0 \hat{A}(b_0 + b_0^\dagger) + \sum_{n=0}^{\infty} \omega_n b_n^\dagger b_n + t_n b_{n+1}^\dagger b_n + t_n b_n^\dagger b_{n+1}$$

Still need to find the orthogonal polynomials

For each choice of scalar product (hence spectral density) these are uniquely determined and there are recursion relations.

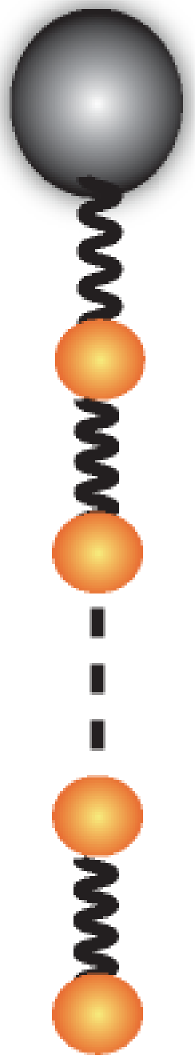
↓ ↓

Numerics: OrthPol determines these and is numerically stable

W. Gautschi, ACM Trans Math Soft. 1994

Analytics: For many spectral densities we know recursions exactly

$$J(\omega) = 2\pi\alpha\omega_c^{1-s}\omega^s e^{-\frac{\omega}{\omega_c}} = \pi h^2(g^{-1}(\omega))\frac{dg^{-1}(\omega)}{d\omega}$$



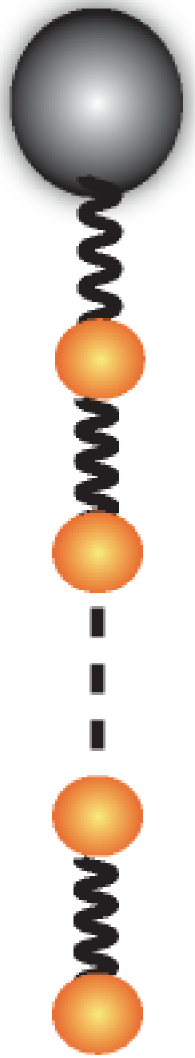
OPs are Laguerre Polynomials

Recurrence coefficients known analytically

$$\omega_n = \omega_c\,(2n + 1 + s)\,,$$

$$t_n = \omega_c\sqrt{(n+1)(n+s+1)}$$

$$J(\omega) = 2\pi\alpha\omega_c^{1-s}\omega^s e^{-\frac{\omega}{\omega_c}} = \pi h^2(g^{-1}(\omega))\frac{dg^{-1}(\omega)}{d\omega}$$



OPs are Laguerre Polynomials

Formulae show that →

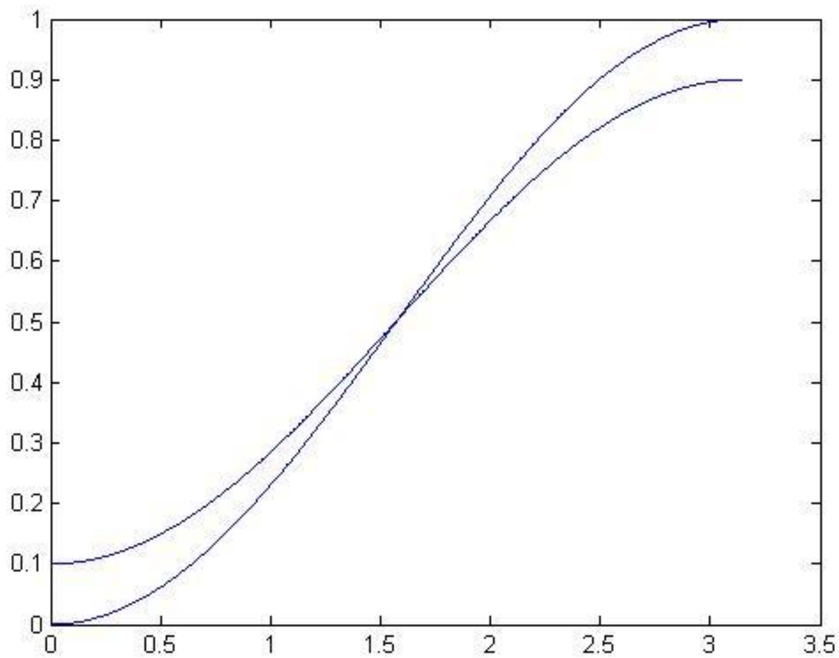
Recurrence coefficients known analytically

$$\lim_{n\to\infty} \epsilon_n \to \frac{\omega_c}{2}$$

$$\lim_{n\to\infty} t_n \to \frac{\omega_c}{4}$$

Physical origin of asymptotic behaviour

Excitations propagate away from system – Irreversibility.



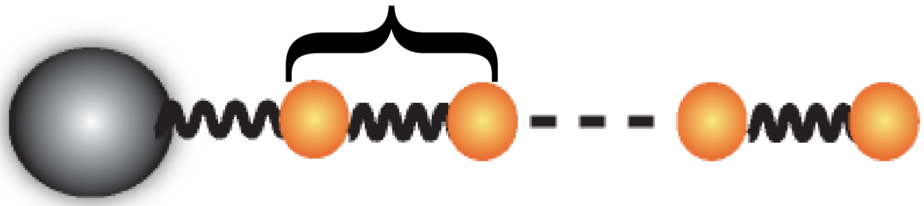
Diagonalise asymptotic chain

$$\omega_k = \frac{\omega_c}{2}(1 - \cos(\pi k))$$

Asymptotic recurrence coefficients give uniform chain with gapless dispersion and bandwidth ω_c

Physical origin of asymptotic behaviour

Encodes spectral density



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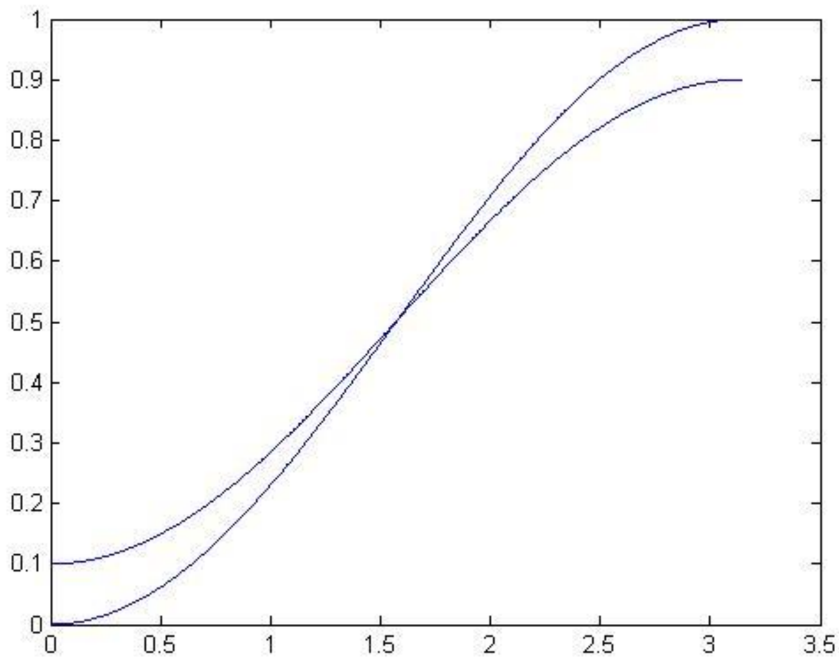

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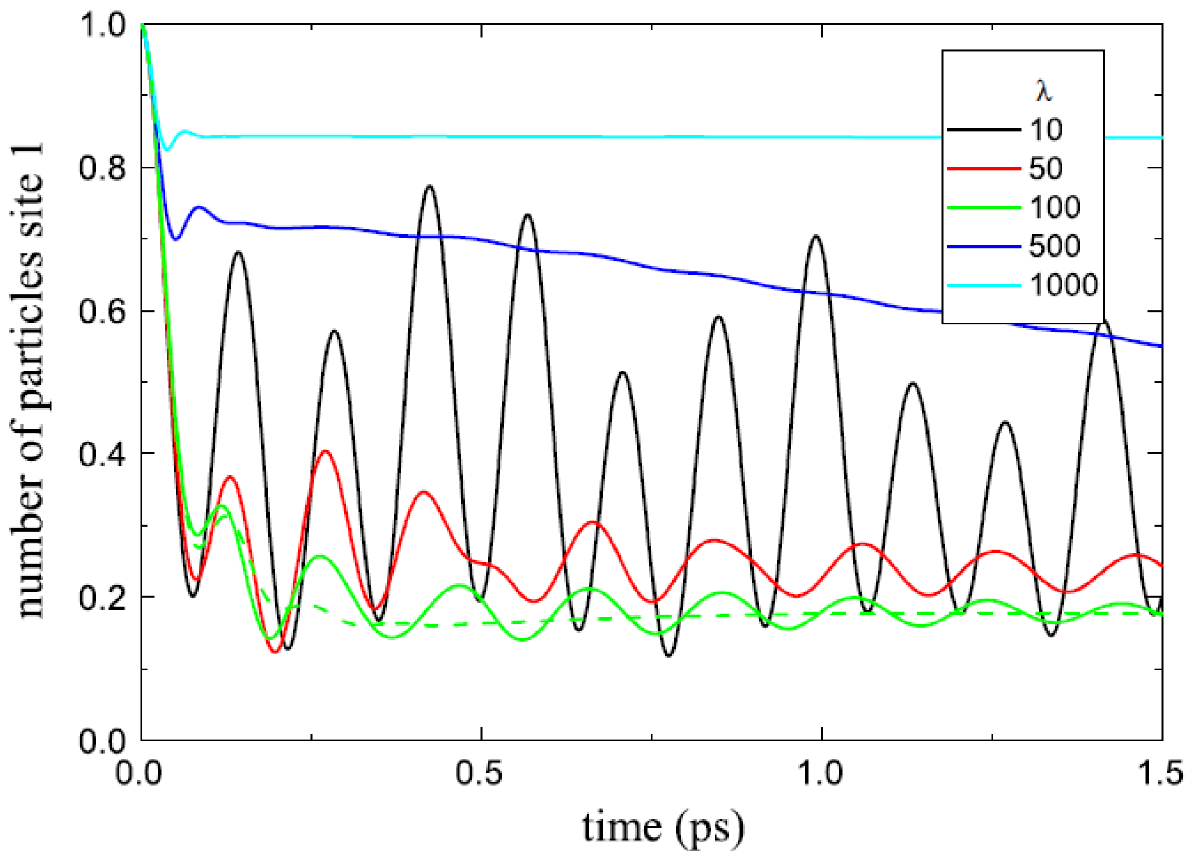
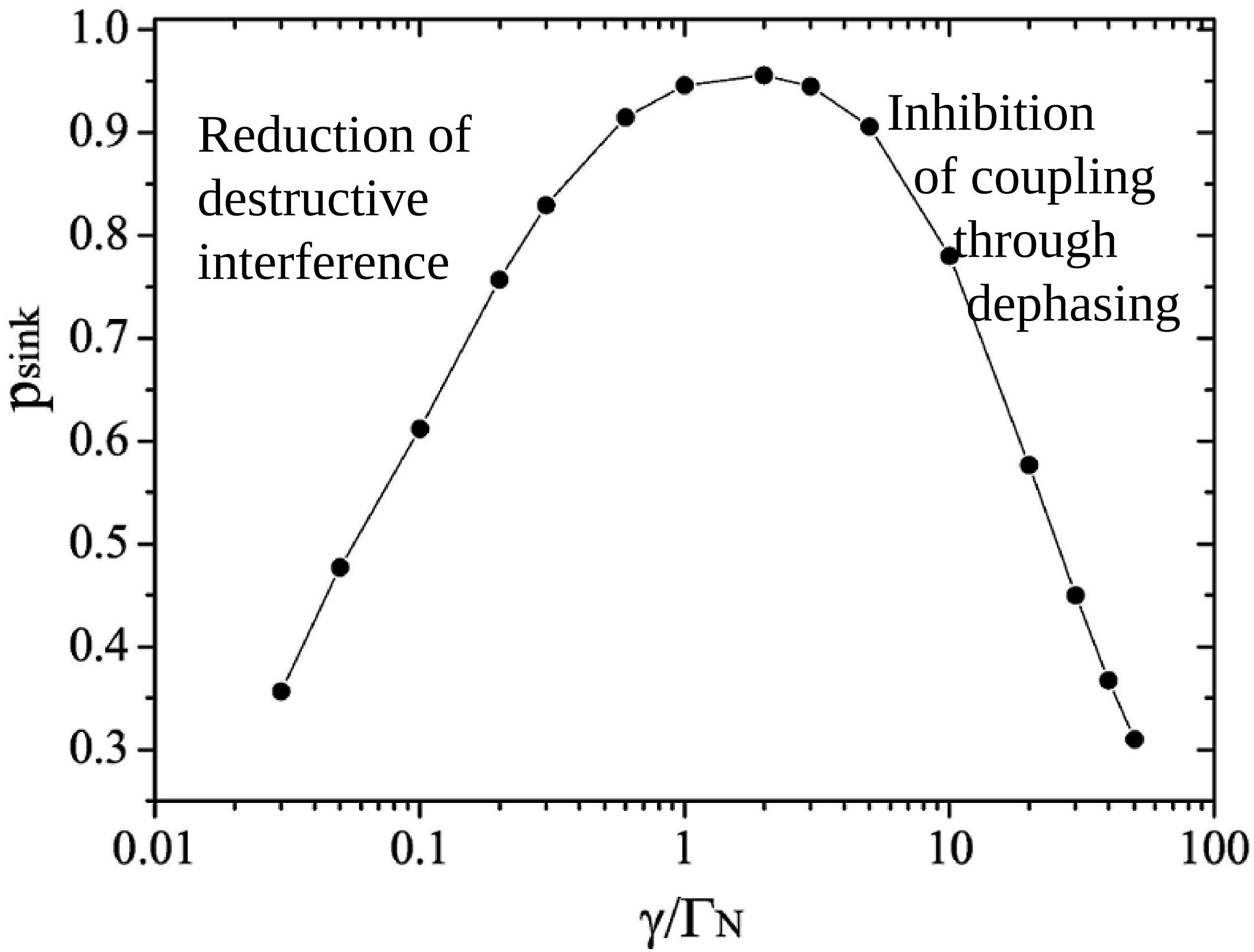


$$J(\omega) = \frac{2\pi\lambda[1000\omega^5 e^{-(\omega/\omega_1)(1/2)} + 4.3\,\omega^5 e^{-(\omega/\omega_2)(1/2)}]}{9!(1000\omega_1^5 + 4.3\omega_2^5)} + 4\pi S_H \omega_H^2 \delta(\omega - \omega_H),$$

Adolphs& Renger 2006

Dependence on Noise Strength

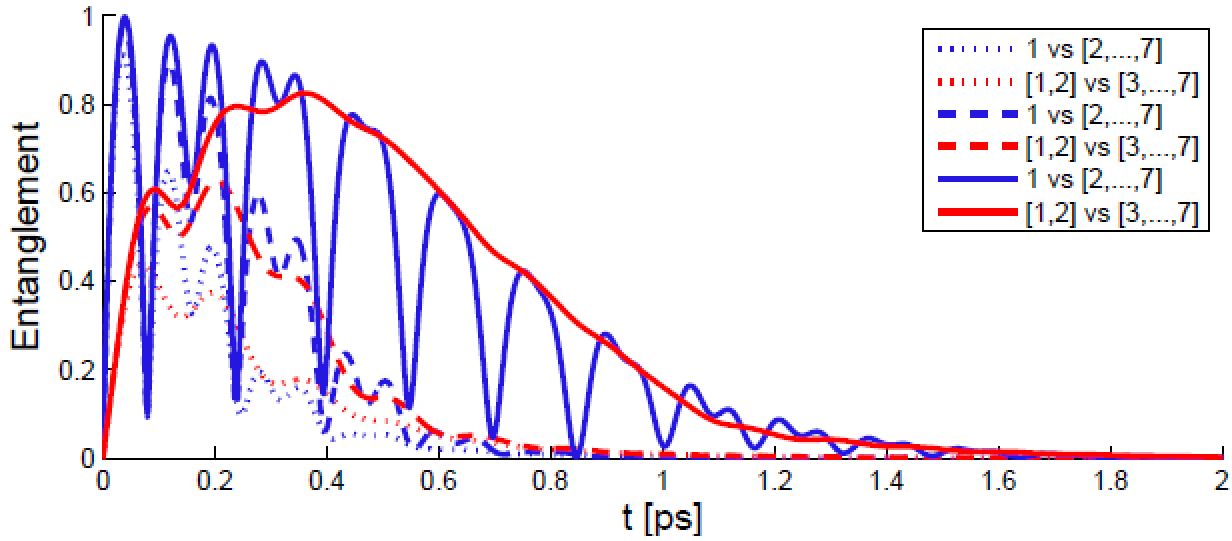


Optimal noise level is such that some coherence surivives

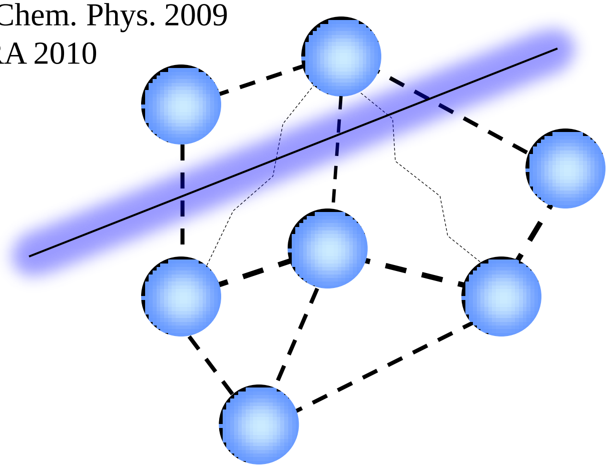
System halfway between quantum and classical world !

Classical versus Quantum: Take I

Quantify entanglement/coherence of states and coherence



Caruso, Chin, Datta, Huelga, Plenio, J. Chem. Phys. 2009
Caruso, Chin, Datta, Huelga, Plenio, PRA 2010
& many colleagues since



Agree on subsystems

Define quantity that decreases under local operations

Draw plot & analyze

Is locality requirement natural here ? Why consider entanglement when dynamics is non-local ?

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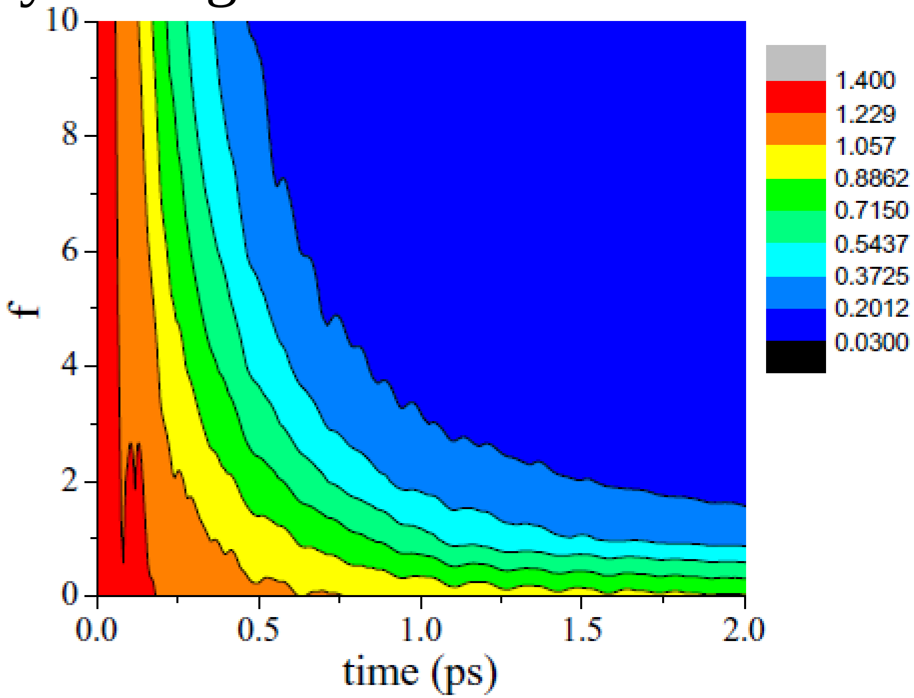

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Consider the power of evolution to generate entanglement.
→ Entangling power

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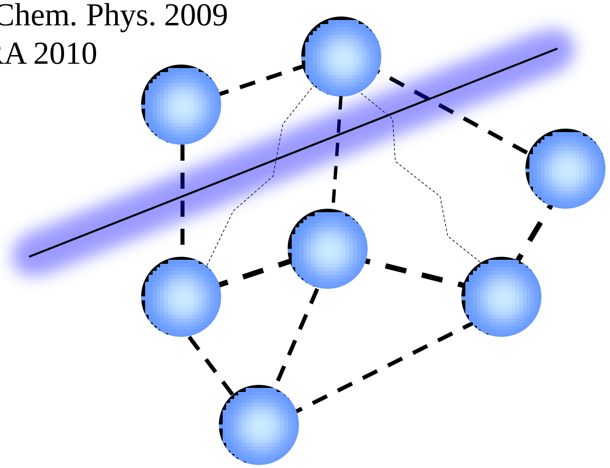
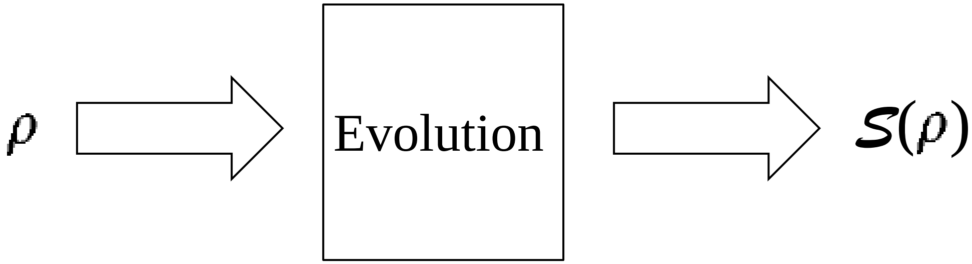


Tutorial Review:
Plenio & Virmani, QIC 2007

Classical versus Quantum: Take II

When is a dynamics classical/quantum ?



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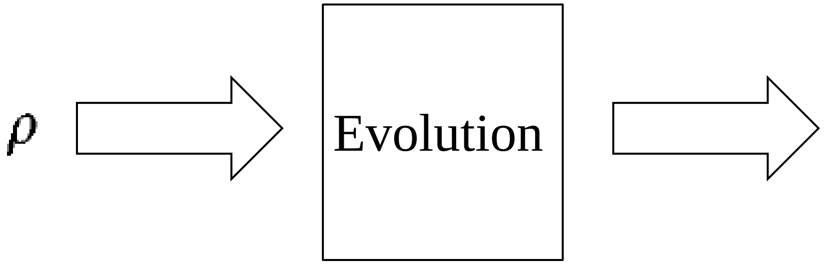

$\mathcal{S}(\rho) = \sum_i \mathrm{tr}[\rho M_i]\sigma_i$

Owari, Serafini, Polzik, Wolf, Plenio, NJP 2008, Nat Phys 2010

Is classical if we can replace box my demon that measures and reprepares the state.

Classical states can be perfectly distinguished and reprepared while quantum states cannot.

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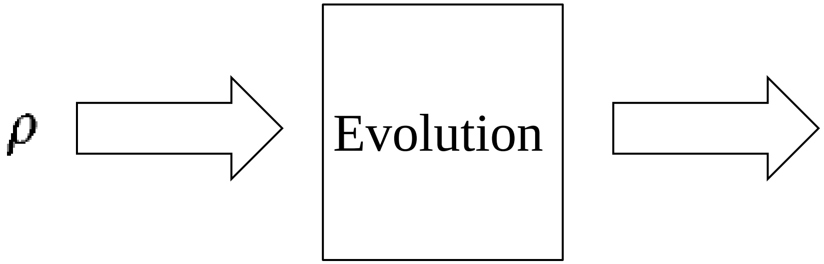

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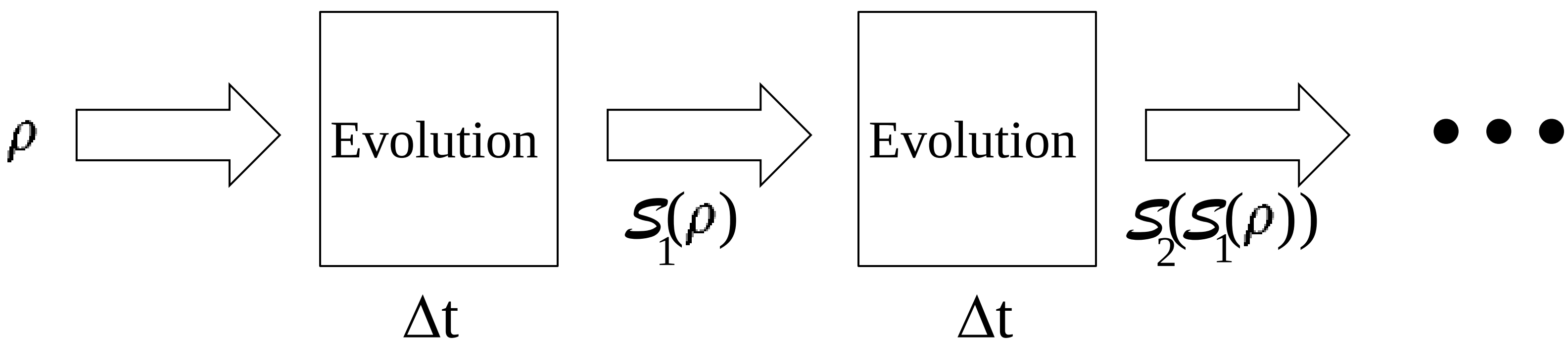
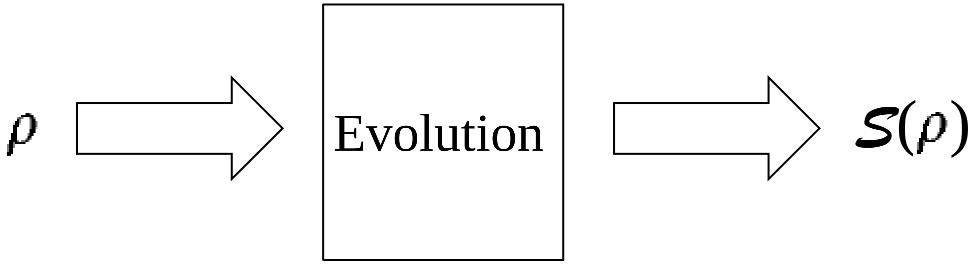


Classical versus Quantum: Take II

When is the action of the environment classical/quantum ?



Classical versus Quantum: Take II

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ρ ⇒ Evolution ⇒ $\mathcal{S}(\rho) = \sum_i U_i \rho U_i^*$

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No quantum correlations are built up with environment and dynamics of environment is classical

Classical versus Quantum: Take II

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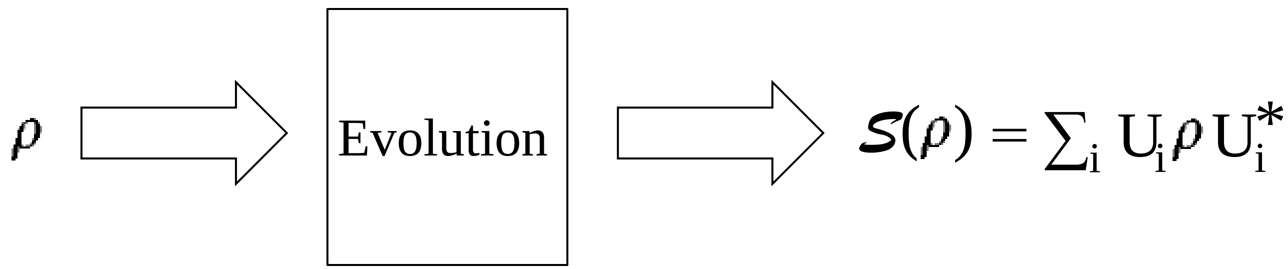

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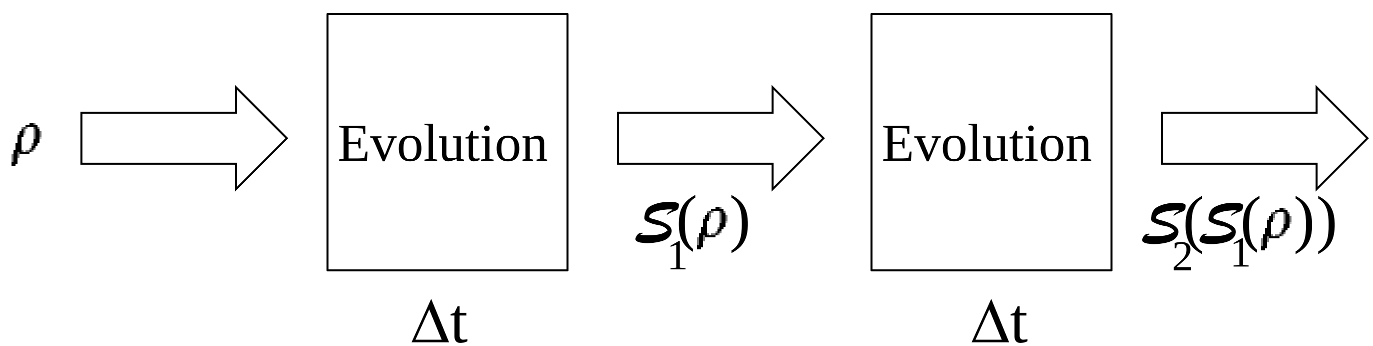

Rivas, Audenaert, Plenio, Huelga, in preparation

Summary

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Optimal performance for intermediate levels of noise, in which master equations or rate equation are inaccurate.

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Develop numerial and analytical methods for this regime from QI & condensed matter

For optimal performance system sits between classical and quantum regime

Quantify entanglement, coherence and quantum character of evolution using QI methods

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