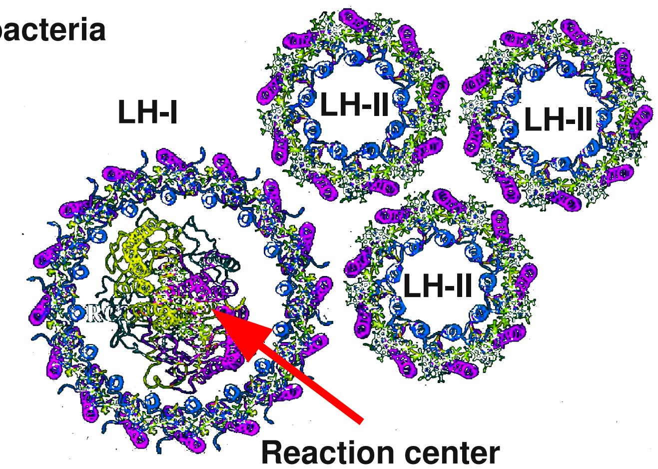
Quantum coherent energy transfer in photosynthesis

Peter Nalbach

First steps of Photosynthesis

Purple bacteria



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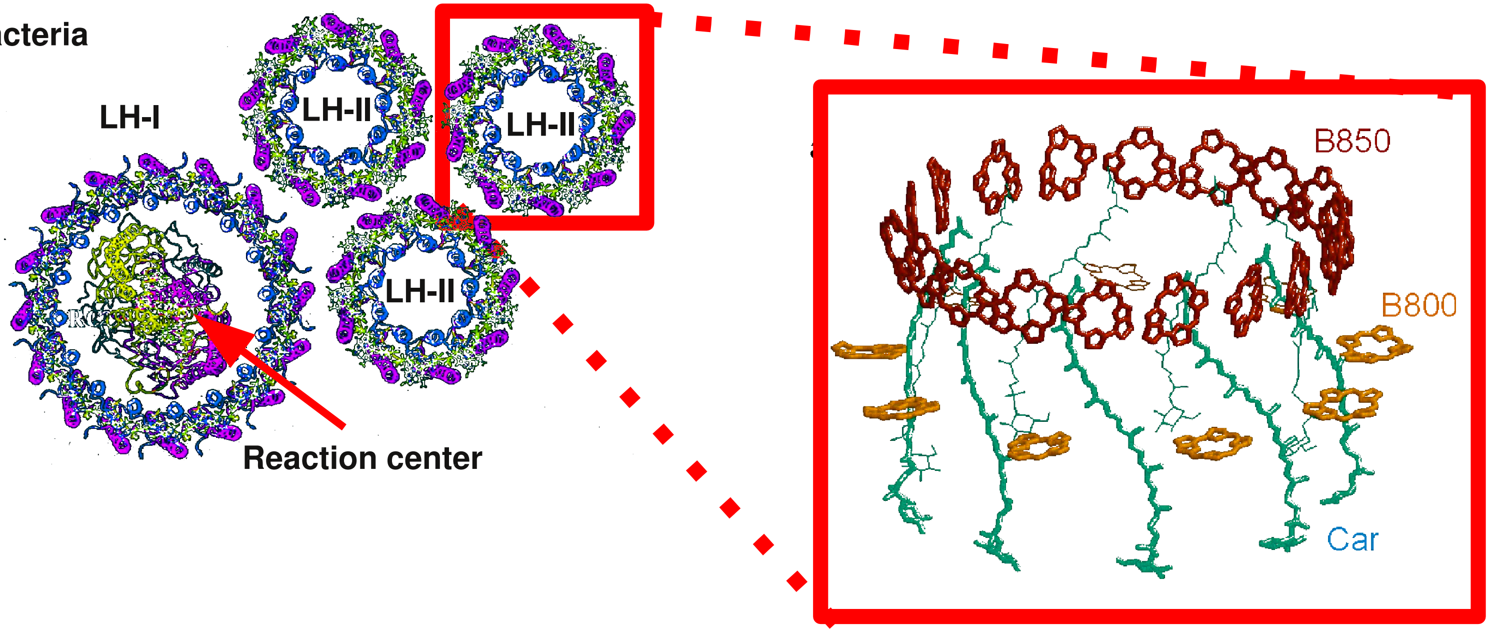

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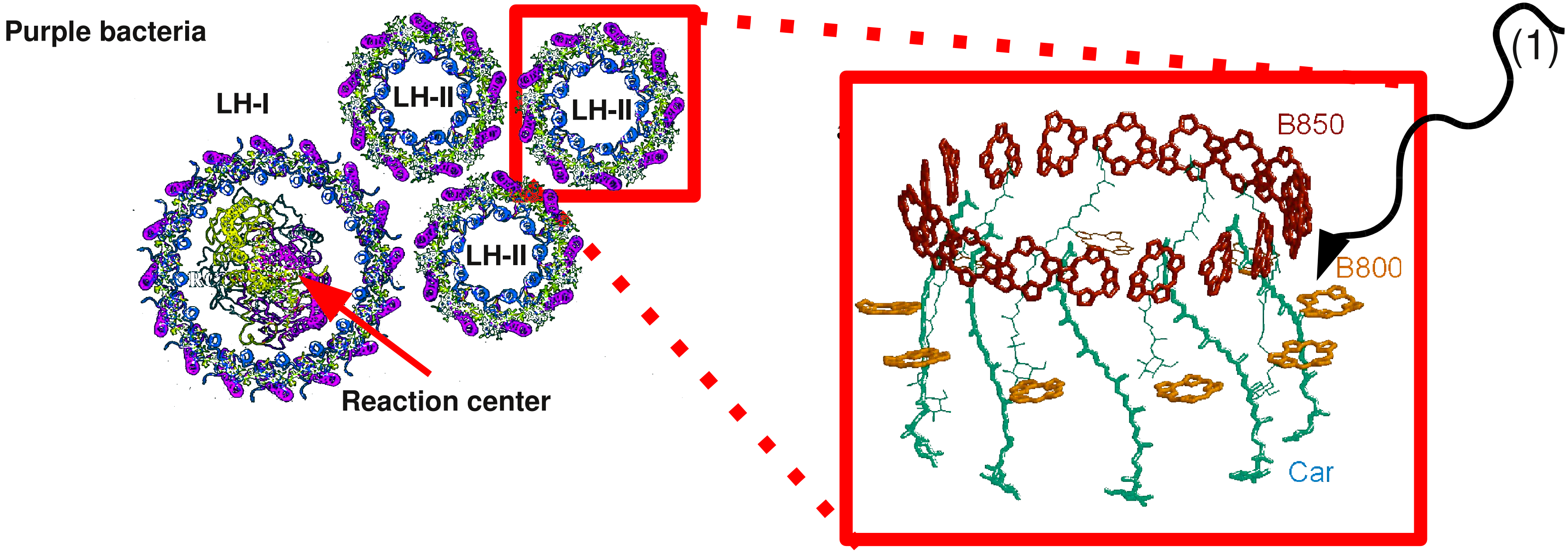

(1) Light is absorbed by chromophores in the antennas → **exciton formation**

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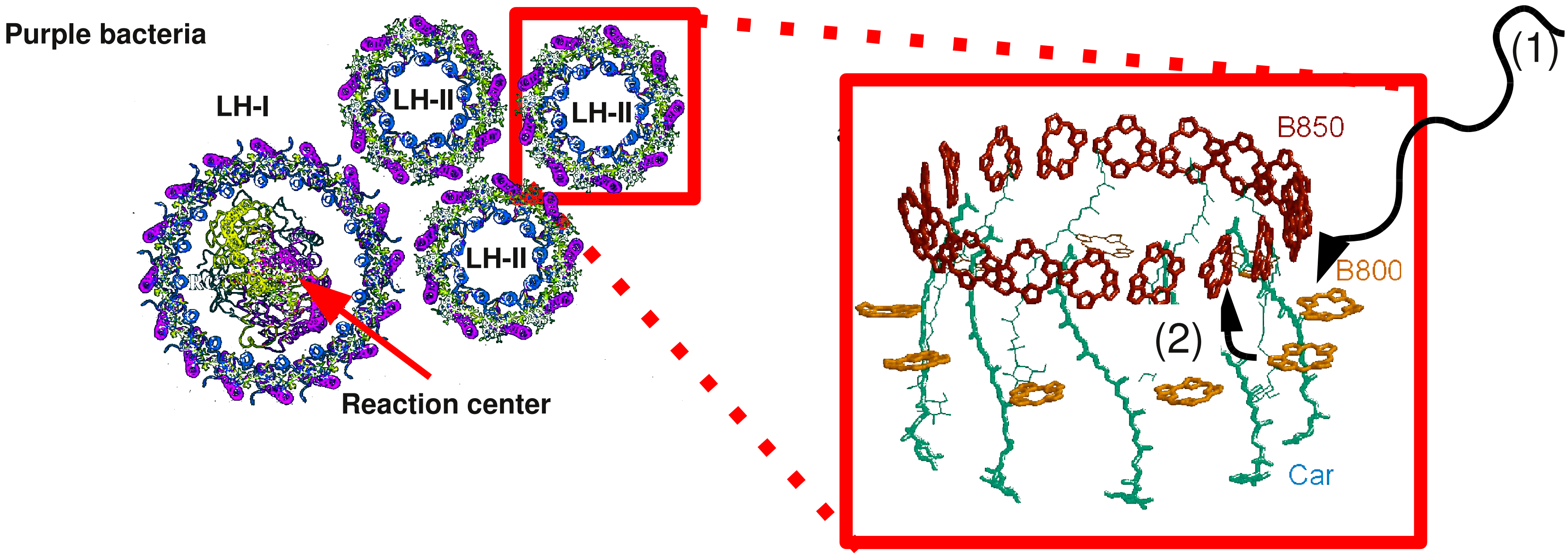

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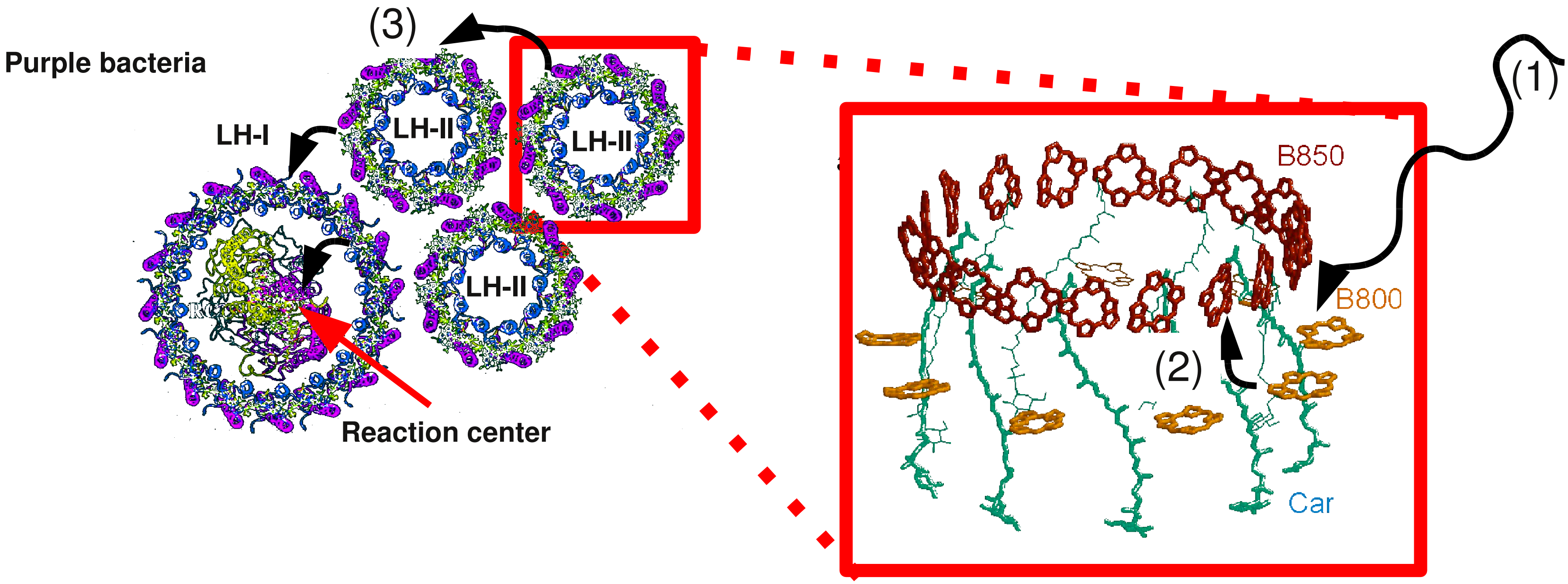

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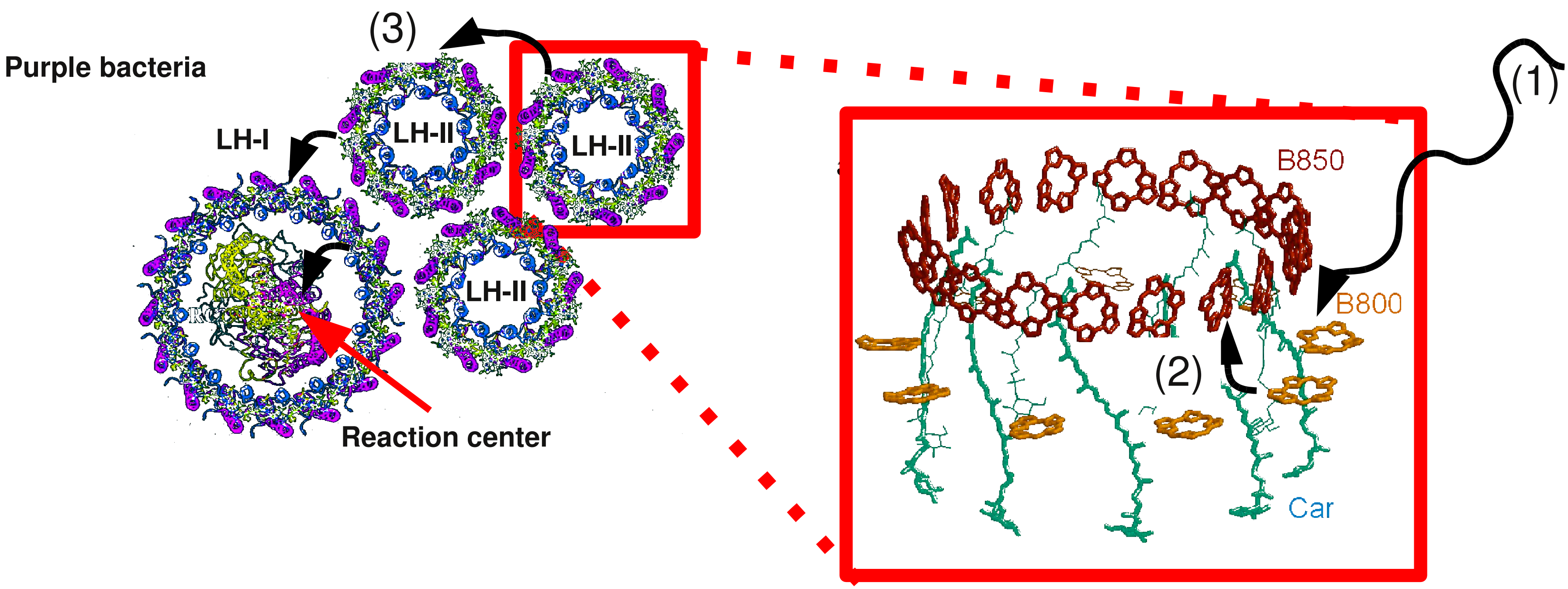

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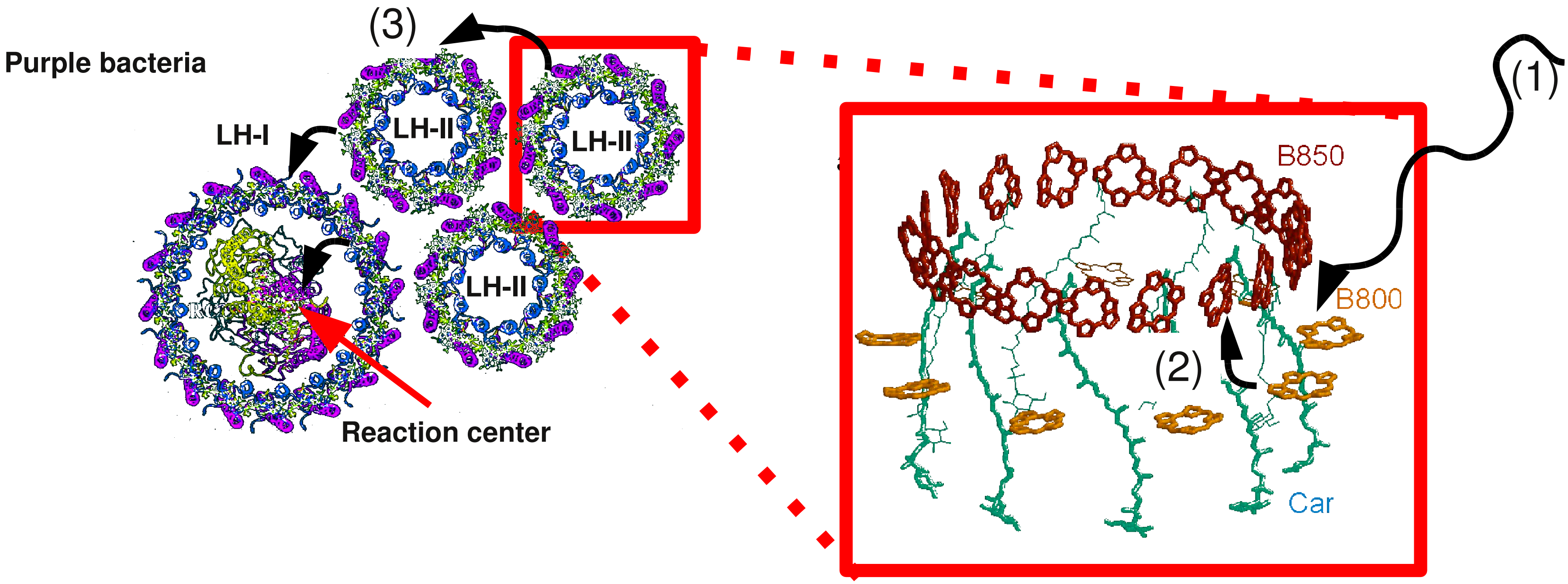
(4) Charges are separated and water get split → **proton production**

First steps of Photosynthesis



(1) Light is absorbed by chromophores in the antennas → exciton formation

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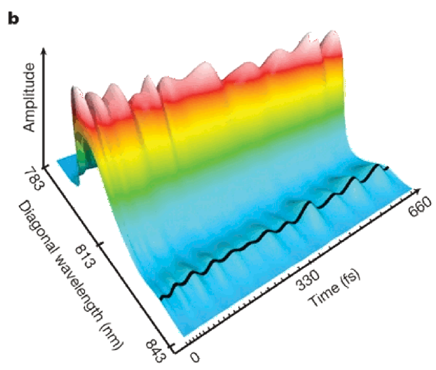
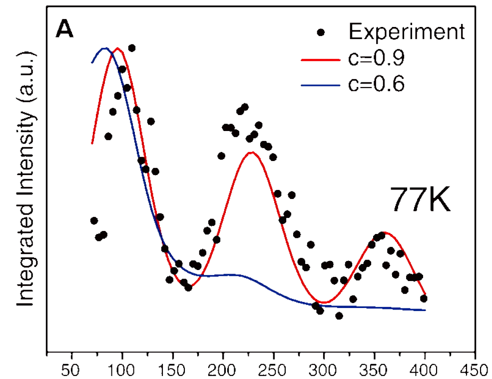
→ Excitonic Energy Transfer without loss !

Green sulfur bacteria



Purple bacteria



Experimental verification of quantum coherence

- Method: ultra-fast spectroscopy
  - 2D photon echos
- System:
  - FMO of green sulfur bacteria (low temperature)
  - (modified) reaction center of purple bacteria (low temperature)
  - LH1 and LH2 of purple bacteria (room temperature)
  - Cryptophyte marine algae (room temperature)

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  $\rightarrow$ This might contribute substantially to **solve the worlds energy problem** since organic solar cells suffer tremendously from inefficient exciton transfer

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- Does Quantum Mechanics serves a purpose within photosynthesis or is it merely a result of energy and length scales ?
  → Did **evolution** use **quantum mechanics** to optimize **biological functions** ?

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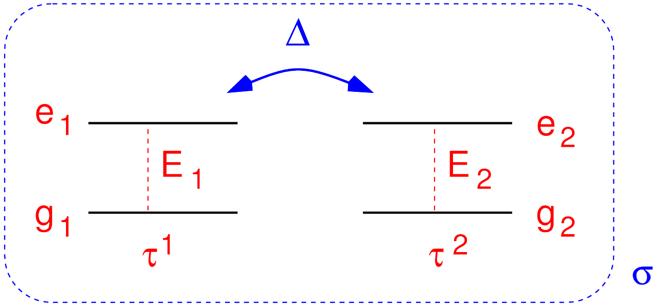
$\rightarrow$ Is this simple argumentation correct ?

Model approach

$$H_{\rm da} = \tfrac{1}{2}\Delta\left\{|1\rangle\langle 2| + |2\rangle\langle 1|\right\} + \sum_{i=1}^{2}|i\rangle\langle i|\sum_k \lambda_k(\mathbf{r}_i)q_k + \tfrac{1}{2}\sum_k\left(p_k^2+\omega_k^2 q_k^2\right)$$

- Donor – Acceptor system
    - Simplest nontrivial model due to coupling to environmental harmonic fluctuations



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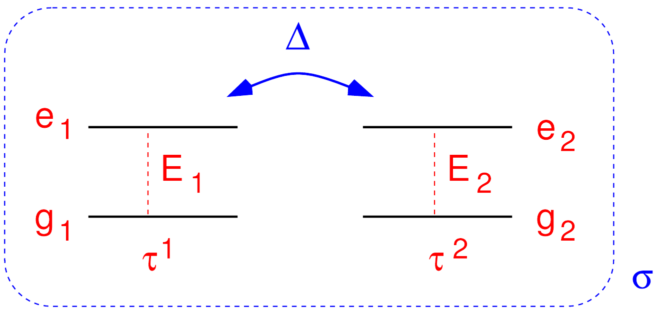

$$J_{ij}(\omega) = \sum_{\vec{k}} \frac{\lambda_{\vec{k}}(\mathbf{r}_i)\lambda_{-\vec{k}}(\mathbf{r}_j)}{2m\omega_k}\delta(\omega-\omega_k) = 2\alpha\omega e^{-\omega/\omega_c}\frac{\sin(\omega t_0)}{\omega t_0} \quad \text{with} \quad t_0 = \frac{r_{ij}}{v}$$

- Localized modes

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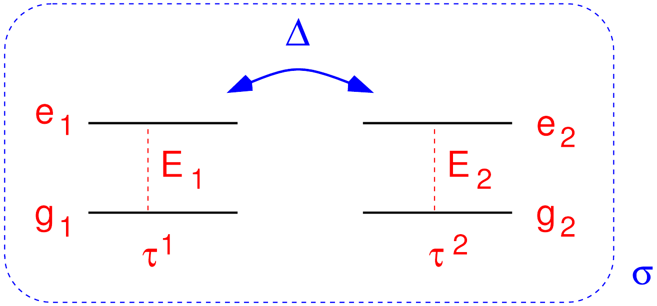

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→ **Attention:** $\omega_c \lesssim \Delta$

Method: Quapi

- Time evolution of statistical operator of donor-acceptor system

$$\langle\sigma^+|\rho_S(t)|\sigma^-\rangle = \left\langle e^{-iHt}\rho_S(0)\rho_B e^{iHt}\right\rangle_{B,\sigma^+,\sigma^-}$$

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- Influence functional

$$I(\sigma^+,\sigma^-,\sigma_1^+,\sigma_1^-,..\sigma_N^-,t) = \exp\left\{-\sum_{j=1}^{N}\sum_{l=0}^{k}\left[\sigma_j^+ - \sigma_j^-\right]\left[\eta_{jl}\sigma_l^+ - \eta_{jl}^\star\sigma_l^-\right]\right\}$$

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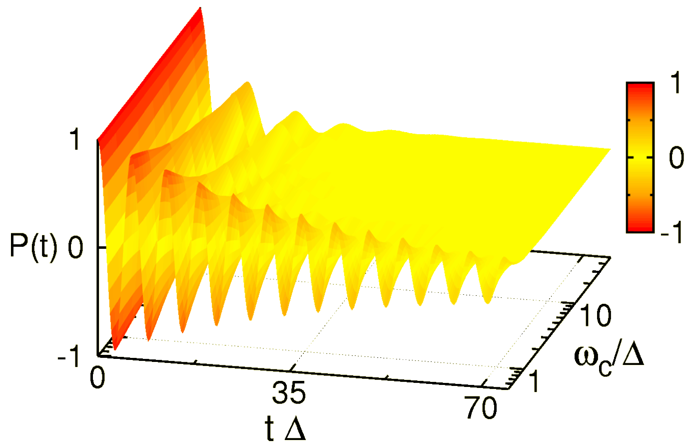
- Memory $\tau = k_{max}\delta t$ and Trotter time δt finite → **numerically exact**

Lessons



- Strong coupling: $\alpha = 0.1$, low temperature: T = 15 K, spatially uncorrelated

M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)
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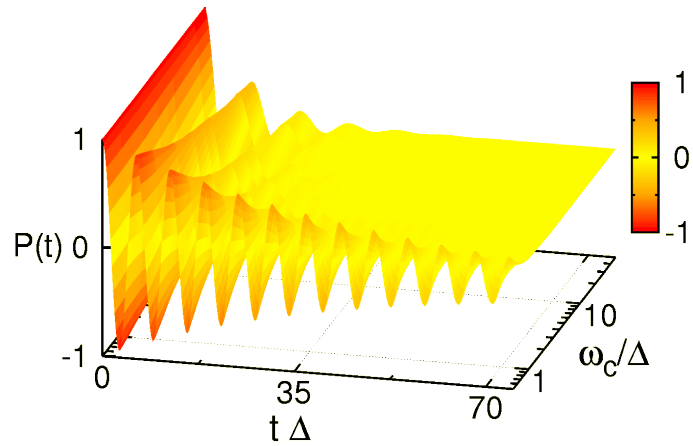

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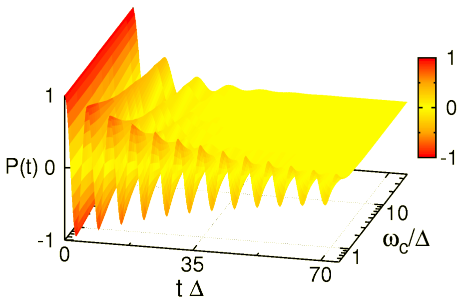

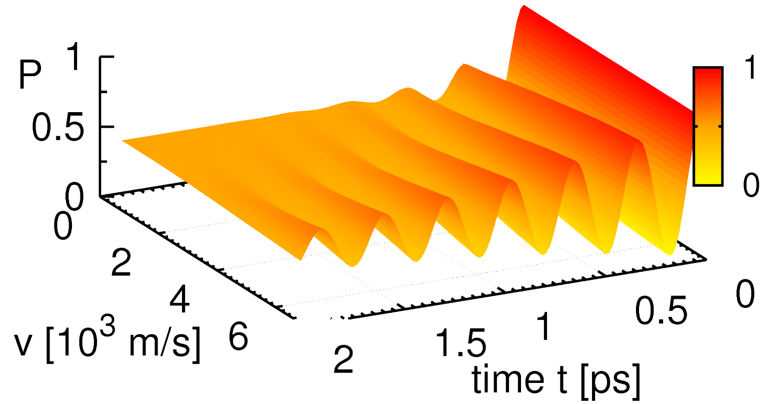

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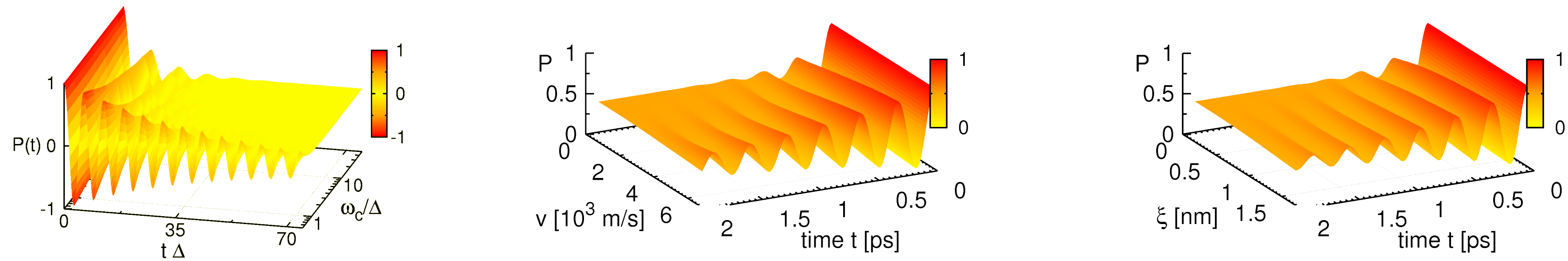

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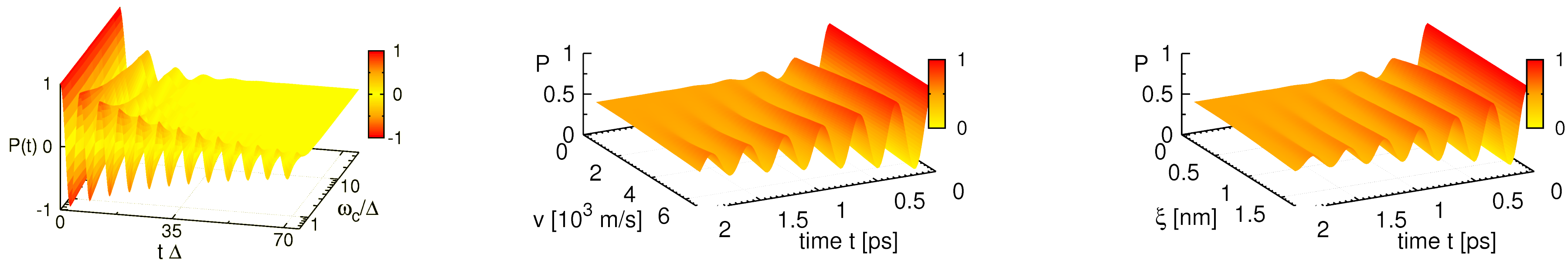

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$\rightarrow$ **Long lived (for ~ 1 ps) quantum coherence is actually not surprising given the fluctuation spectrum and/or reasonable spatial correlations**

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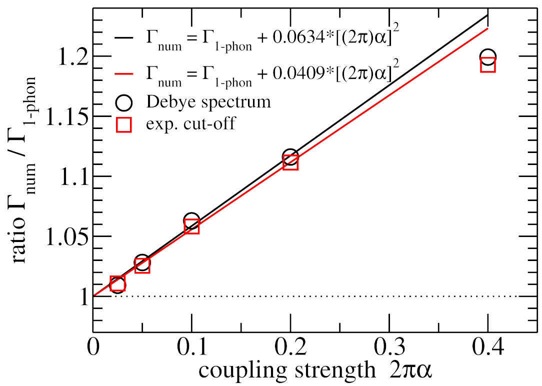
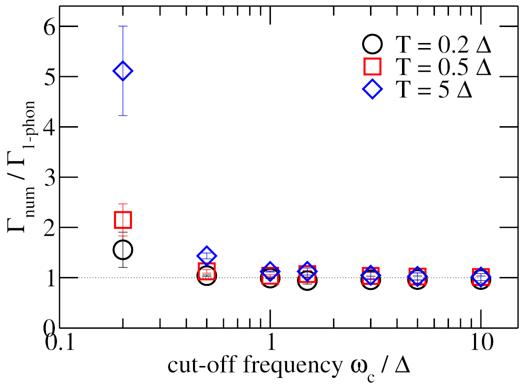
Never underestimate small ω_c !





- Comparison at weak coupling of QUAPI with RESPET

P. Nalbach and M. Thorwart, J. Chem. Phys. 132, 194111 (2010)
→ selected for the June 1, 2010 issue of Virtual Journal of Biological Physics Research
P. Nalbach, Phys. Rev. B 66, 134107 2002

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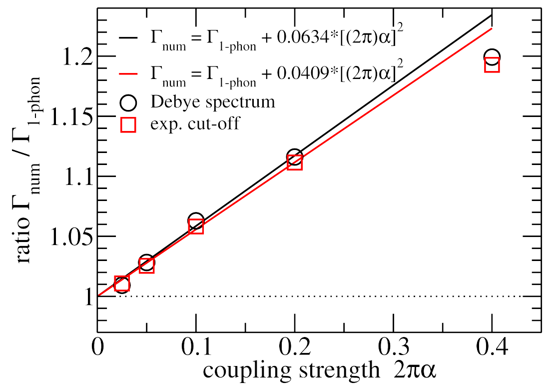
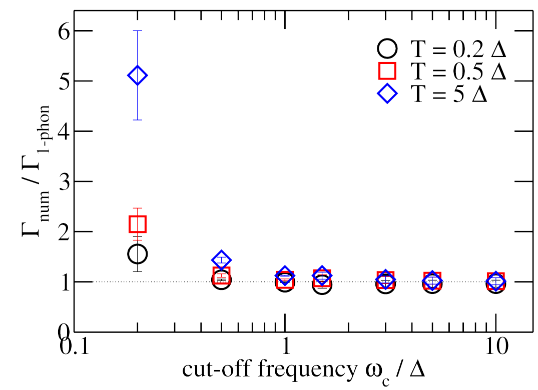
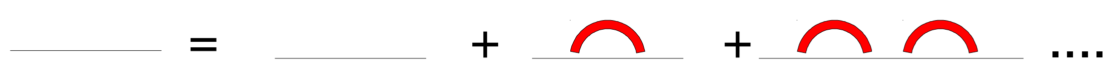




- Comparison at weak coupling of QUAPI with RESPET
  - RESPET (resumed perturbative treatment)
    - Memory kernel exact to second order (including all non-Markovian features)
    - Time evolution operator 

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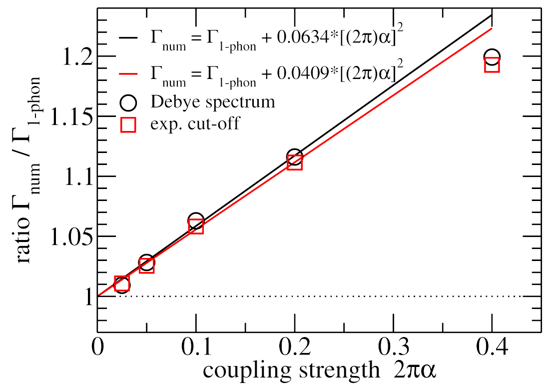

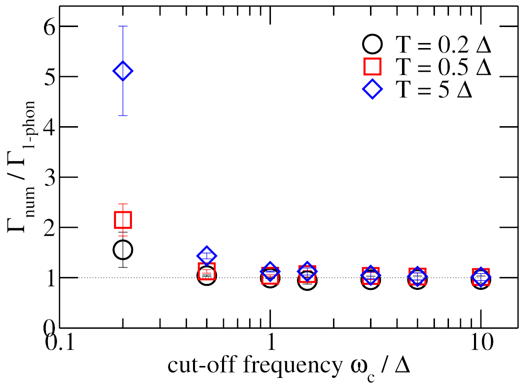

- Comparison at weak coupling of QUAPI with RESPET
  - RESPET (resumed perturbative treatment)

→ Multi-phonon processes dominate !
→ Lindblad, Redfield, Markov ... questionable !!

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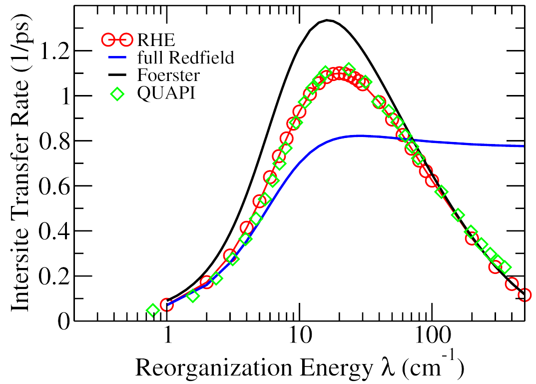
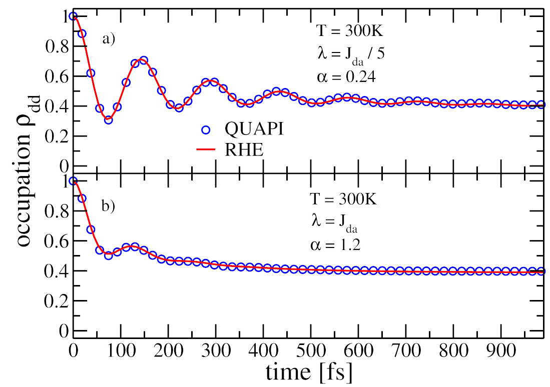
Small ω_c – Check of method





- Comparison of QUAPI with reduced hierachy equations
  → joint project with A. Ishizaki and G.R. Fleming
  - Left: ε_a-ε_d = 100 cm^{-1}, Δ = 40 cm^{-1}, ω_c = 53 cm^{-1} , T = 300 K
  - Right: ε_a-ε_d = 100 cm^{-1}, Δ = 200 cm^{-1}, ω_c = 53 cm^{-1} , T = 300 K

P. Nalbach, A. Ishizaki, G.R. Fleming and M. Thorwart, under preparation,
Efficient theoretical methods for the dissipative biomolecular exciton transport

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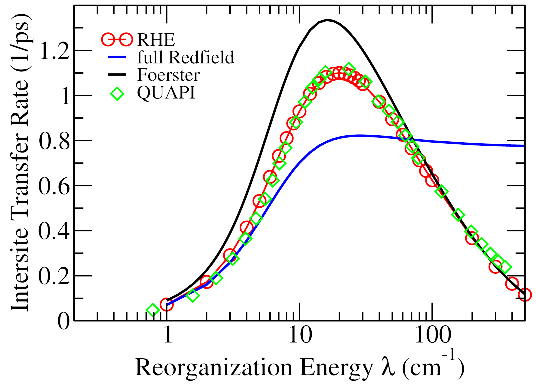

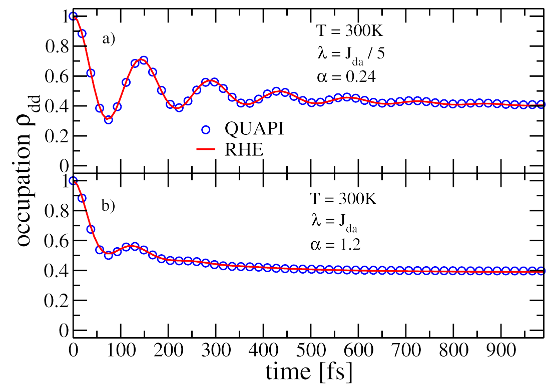

- Comparison of QUAPI with reduced hierachy equations
  → joint project with A. Ishizaki and G.R. Fleming

→ **Both methods give identical results for typical parameters of biomolecular exciton transfer**

P. Nalbach, A. Ishizaki, G.R. Fleming and M. Thorwart, under preparation,
Efficient theoretical methods for the dissipative biomolecular exciton transport

Why quantum coherence ? Function ?

- Long lived (for ~ 1 ps) quantum coherence is actually not surprising
  - → Does it serve a purpose ?
  - → Are there biological functions relying on quantum coherence ?
  - → Did evolution drive nature to facilitate quantum coherence ?

P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules

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  High efficiency in exciton transfer to RC caused by quantum coherence !

  → caused intensive research effort:
  - Plenio group
  - Aspuru-Guzik group

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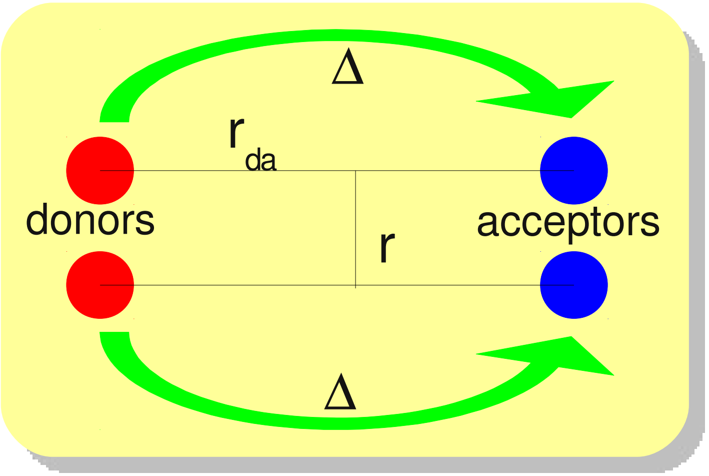
→ No final answer yet

P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules

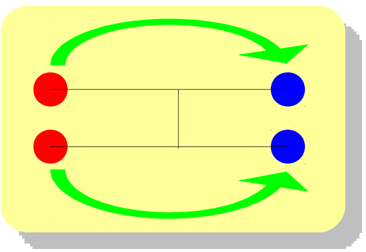
Lessons for functions from models

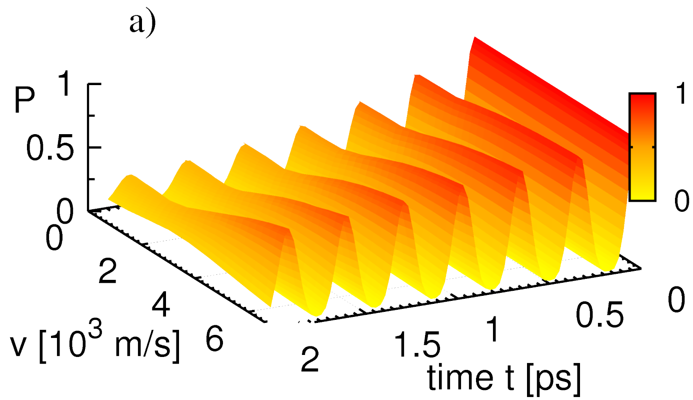


- $\alpha = 0.04$, $\omega_c = \Delta = 106$ cm^{-1}, T = 15.2 K
- Correlated fluctuations:
  - (a) distant channels: r_{da} = 3.8 Å, r = 38 Å
  - (b) close channels: r_{da} = 38 Å, r = 3.8 Å

P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules

Lessons from multiple path





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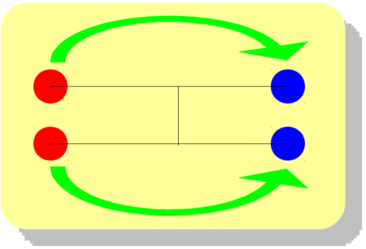

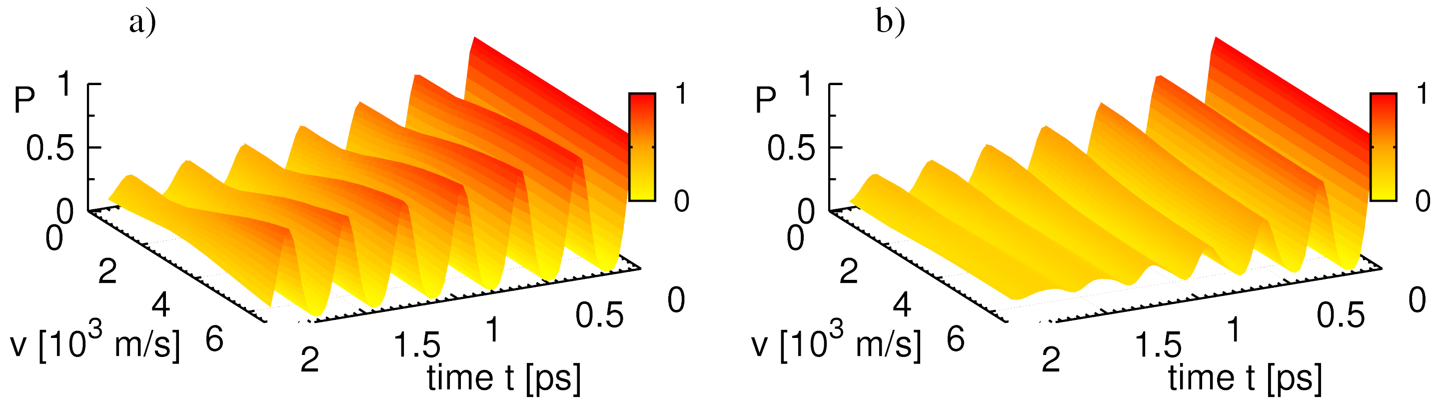

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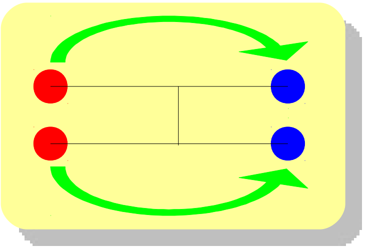
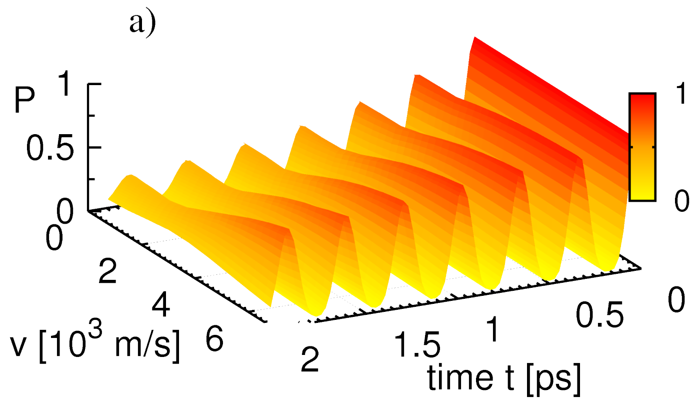
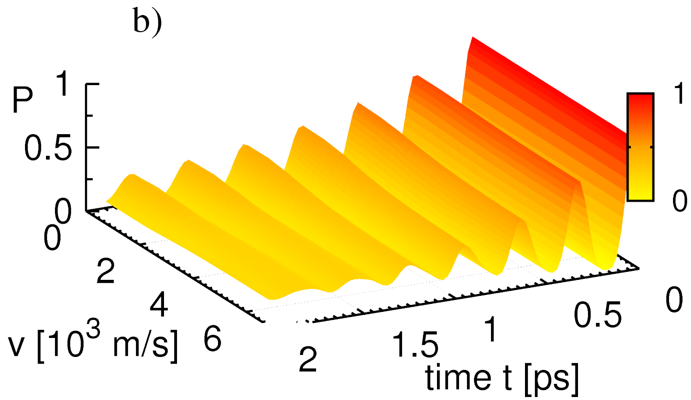
  - (b) close channels: r_{da} = 38 Å, r = 3.8 Å
    → communicating, but suppressed at room temperatures

P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules

Lessons from multiple path





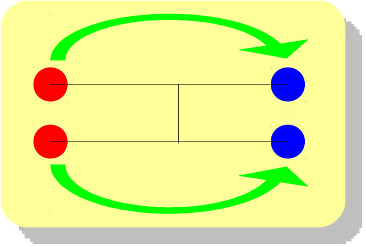


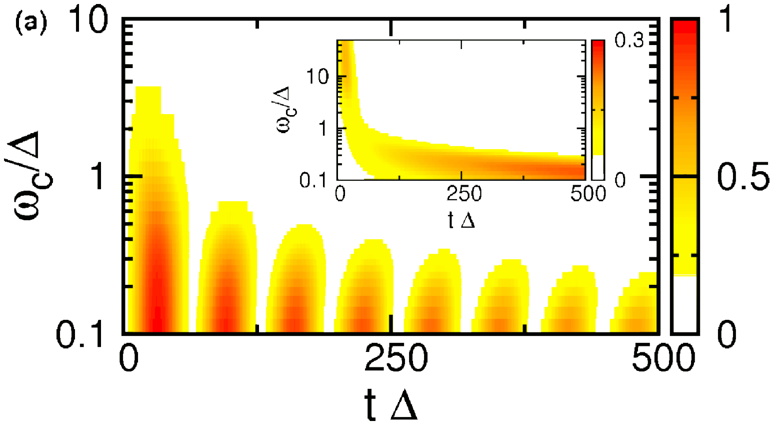
- $\alpha = 0.04$, $\omega_c = \Delta = 106\ cm^{-1}$, T = 15.2 K
- Correlated fluctuations:
  - (a) distant channels: r_{da} = 3.8 Å, r = 38 Å → independent
  - (b) close channels: r_{da} = 38 Å, r = 3.8 Å
    → communicating, but suppressed at room temperatures

→ Spatial correlated fluctuations can enhance and suppress decoherence

P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules

Lessons from multiple path



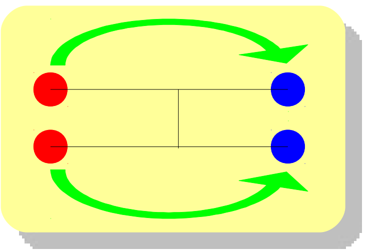


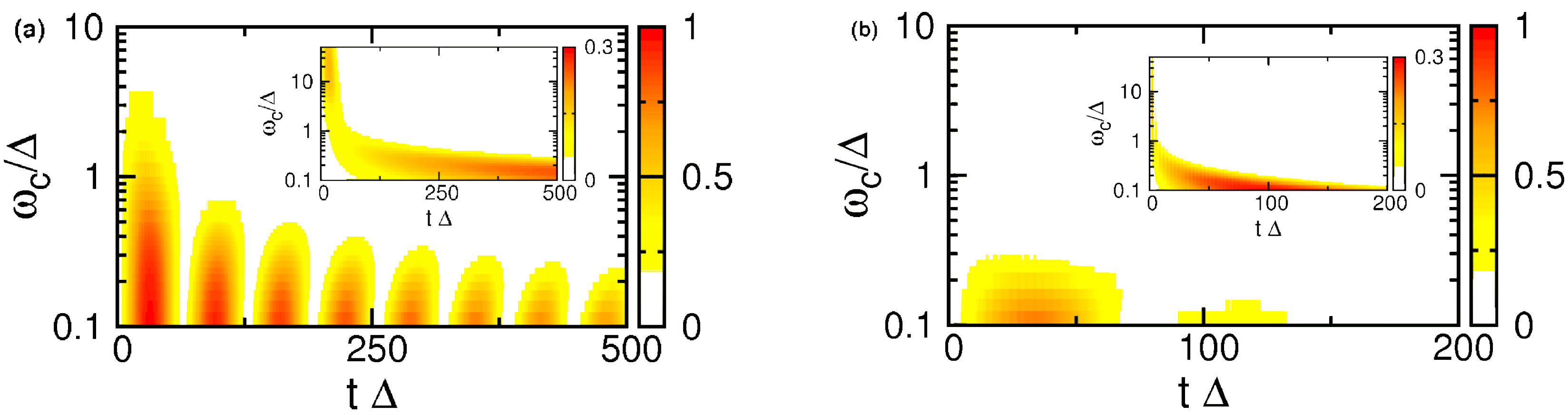
Negativity as entanglement measure in close channels:

- $\Delta = 106\ \mathrm{cm}^{-1}$, T = 15.2 K, (a) $\alpha = 0.01$
- main: coupled donor-acceptors: J = 0.1 Δ
- Inset: uncoupled: J = 0

M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)

Lessons from multiple path



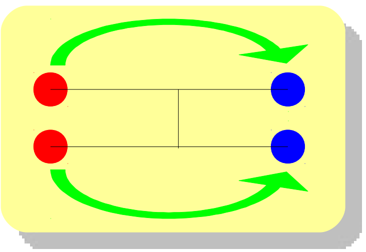


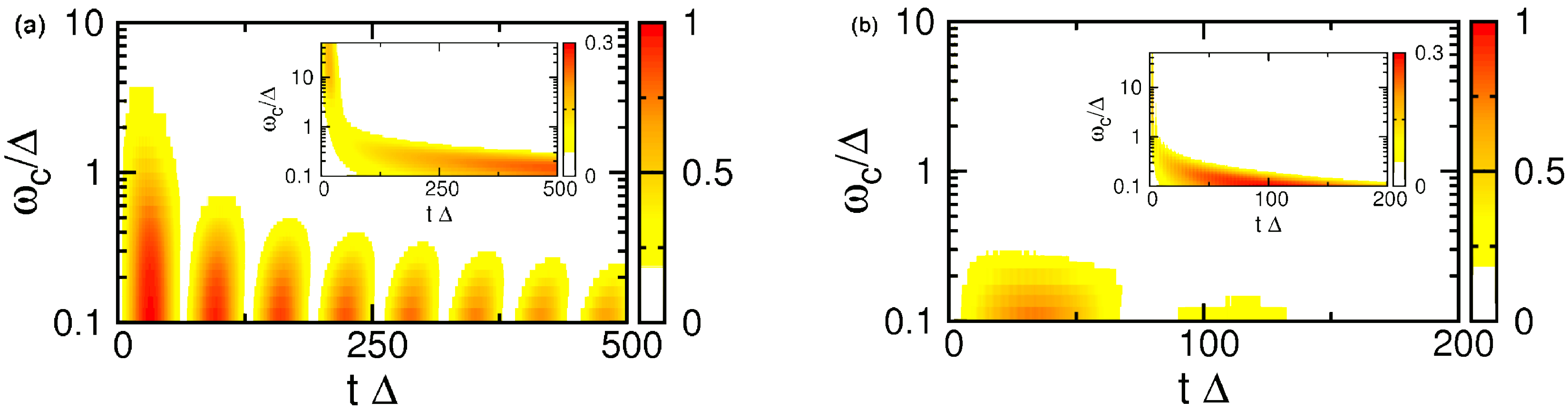
Negativity as entanglement measure in close channels:

- $\Delta = 106$ cm^{-1}, T = 15.2 K, (a) $\alpha = 0.01$ and (b) $\alpha = 0.1$
- main: coupled donor-acceptors: J = 0.1 Δ
- Inset: uncoupled: J = 0

M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)

Lessons from multiple path





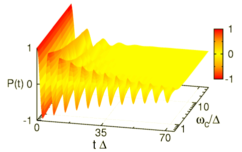
Negativity as entanglement measure in close channels:

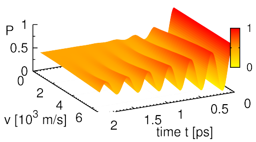
- $\Delta = 106$ cm^{-1}, T = 15.2 K, (a) $\alpha = 0.01$ and (b) $\alpha = 0.1$
- main: coupled donor-acceptors: J = 0.1 Δ
- Inset: uncoupled: J = 0

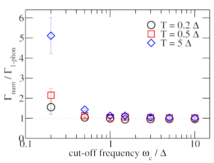
→ Slow bath supports (re-) emergence and death of entanglement and even generates entanglement for uncoupled channels

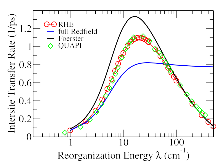
M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)

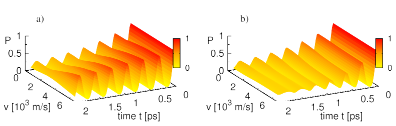
Summary

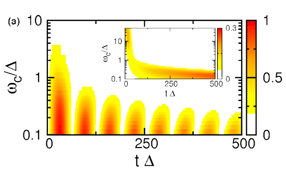












- Long lived quantum coherence can be understood
  - for slow environmental fluctuations and

    M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)
  - spatially correlated environmental fluctuations

    P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules
- Multi-phonon processes dominate rendering Lindblad, Redfield, Markov (...) questionable

  P. Nalbach and M. Thorwart, J. Chem. Phys. 132, 194111 (2010)

  → selected for the June 1, 2010 issue of Virtual Journal of Biological Physics Research
- All methods must be tested carefully: Quapi = RHE

  P. Nalbach, A. Ishizaki, G.R. Fleming and M. Thorwart, under preparation
- Spatially correlated fluctuations can enhance and suppress decoherence in multiple channel configurations

  P. Nalbach, J. Eckel and M. Thorwart, New J. of Phys. Focus issues: Quantum effects and noise in biomolecules
- Slow bath supports (re-) emergence and death of entanglement and even generates entanglement for uncoupled channels

  M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach, S. Weiss, Chem. Phys. Lett. 478, p. 234-237 (2009)

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  - Dr. Jens Eckel, Bundesamt für Reaktorsicherheit
  - Dr. Stephan Weiss, Niels-Bohr-Institute, Kopenhagen
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  - Prof. G.R. Fleming, UC Berkeley
  - Prof. John Henry Reina, Cali, Kolumbien
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