Transport Efficiency in Open Quantum Systems with Static and Dynamic Disorder

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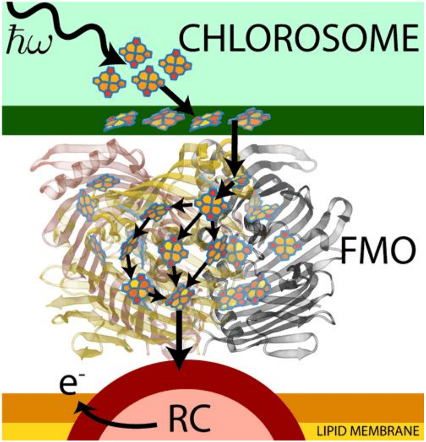
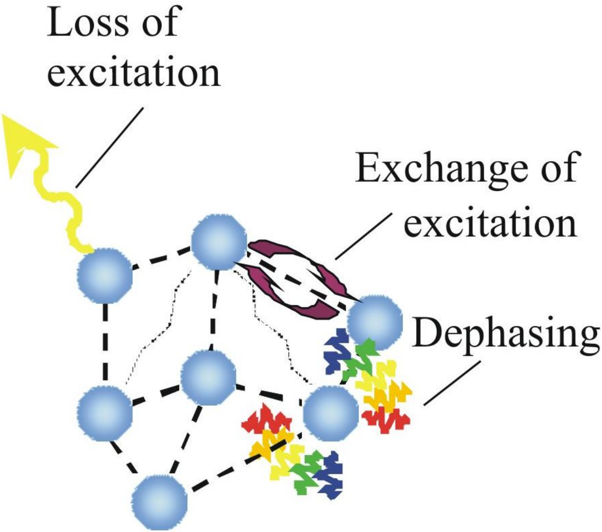
Quantum Coherence in Fenna-Matthews-Olson Complex

- Quantum coherence in photosynthetic light-harvesting systems (e.g. FMO complex), even at room temperature
- Under what circumstances can nature preserve quantum coherence in macromolecules in a wet and hot environment?
- What, if any, is functional purpose of quantum coherence in natural systems?
- General lessons?

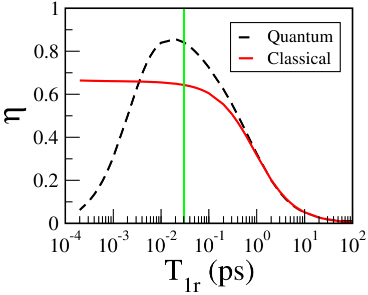


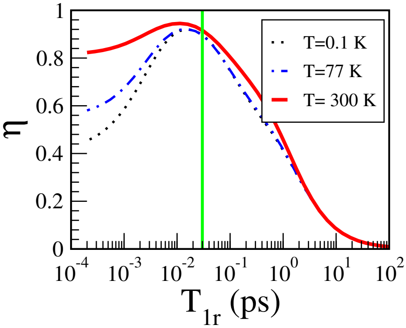
FMO as Open Disordered System with Dephasing



Importance of Opening in FMO

- Celardo et al (2012): Quantum transport enhancement in FMO depends strongly on opening (coupling to reaction center, which serves as sink)
- Peak quantum efficiency occurs near superradiance transition (segregation of decay widths due to opening)





- Quantum efficiency may *increase* with T (up to a point) – noise-assisted transport (e.g Plenio & Hulega, 2008)

Broader Perspective

- Need systematic understanding of quantum transport in situations where all of the following may simultaneously be important:
  1. Disorder
  2. Opening
  3. Finite temperature / decoherence
- Work in single excitation regime – tight binding models
- Applications include quantum dot arrays and lattices, J-aggregates, natural photosynthetic complexes, artificial light-harvesting systems, bio-engineered devices for photon sensing, quantum information processing, ...

Questions Include:

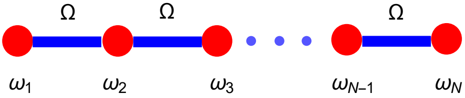
- Under what generic conditions can coherent effects enhance transport in open quantum systems?
- For which values of the opening strength are coherent effects relevant?
- When can a non-zero temperature (dephasing) enhance quantum transport in open system?
- How do system size and connectivity affect quantum transport?

Quantum Network – Tight Binding Model

Closed system described by single-excitation Hamiltonian

E.g. a linear chain

$\omega_j \in [-W/2, W/2]$



$$\mathrm{H_{sys}} = \sum_{j=1}^{N} \omega_j \left| j \right\rangle \left\langle j \right| + \Omega \sum_{j=1}^{N-1} \left(\left| j \right\rangle \left\langle j+1 \right| + \left| j+1 \right\rangle \left\langle j \right| \right)$$

Opening up system gives rise to non-Hermitian effective Hamiltonian

$$H_{\mathrm{eff}}(E) = \mathrm{H_{sys}} - iQ(E)/2 + \Delta(E)$$

$$Q_{j,k}(E) = 2\pi \sum_c A_j^c(E) A_k^c(E)^* \rho^c(E) \qquad \Delta_{j,k}(E) = \sum_c P.V. \int dE' \frac{A_j^c(E') A_k^c(E')^* \rho^c(E')}{E - E'}$$

$A_j^c(E)$ is coupling of site j to continuum channel c

$\rho^c(E)$ is continuum density of states

Quantum Network – Incorporating Openness

Opening up system gives rise to non-Hermitian effective Hamiltonian

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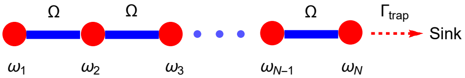
In practice, convenient to approximate with energy-independent effective Hamiltonian (matrix)

$$H_{\text{eff}} = \mathrm{H}_{\text{sys}} - iQ(E_0)/2$$

- Valid for broad-banded continuum spectrum
- Opening may be small or large
- Same approximation as Fermi Golden Rule (for one channel)

Quantum Network – Incorporating Openness

Example: Linear Chain with Openness



- Site N coupled to reaction center (rate Γ_{trap})
- Excitation on any site may decay through recombination (rate Γ_{fl})

$$(H_{\mathrm{eff}})_{j,k} = \omega_j \delta_{j,k} + \Omega \left(\delta_{j,k+1} + \delta_{j,k-1} \right) - \frac{i}{2} \left(\Gamma_{\mathrm{trap}} \delta_{j,N} + \Gamma_{\mathrm{fl}} \right) \delta_{j,k}$$

Finite Temperature Effects

Cannot work with quantum states
$\Rightarrow$ Need density matrix formalism

Quantum master equation

$$\dot{\rho}(t) = -\mathcal{L}_{\text{tot}}\, \rho(t)$$

$$\mathcal{L}_{\text{tot}} = \mathcal{L}_{\text{sys}} + \mathcal{L}_{\text{trap}} + \mathcal{L}_{\text{fl}} + \mathcal{L}_{\text{deph}}$$

$$\left(\mathcal{L}_{\text{sys}} + \mathcal{L}_{\text{trap}} + \mathcal{L}_{\text{fl}}\right) \rho = i\, [\mathrm{H}_{\text{sys}}, \rho] + \frac{\Gamma_{\text{trap}}}{2} \left\{ |N\rangle \langle N| \, , \rho \right\} + \Gamma_{\text{fl}} \rho$$

Simplest dephasing operator: Haken-Strobl-Reineker (HSR) model

$$\left(\mathcal{L}_{\text{deph}} \rho\right)_{j,k} = \gamma \rho_{jk} \left(1 - \delta_{j,k}\right)$$

$$\text{i.e.} \quad \dot{\rho}_{jk} = \ldots - \gamma \rho_{jk} \ \text{ for } \ j \neq k \qquad [\gamma \sim \text{temperature}]$$

Integrating Master Equation

In general must numerically integrate $\dot{\rho}(t) = -\mathcal{L}_{\text{tot}}\,\rho(t)$, starting from $\rho(0)$

In practice, often interested in efficiency:

$\eta =$total probability of successfully ending up in the trap

$$\eta = \Gamma_{\text{trap}} \int_0^\infty \rho_{NN}(t)\,dt = \Gamma_{\text{trap}}(\mathcal{L}_{\text{tot}}^{-1}\rho(0))_{\text{NN}}$$

... or in transfer time:

$\tau =$average time to reach the trap

$$\tau = \frac{\Gamma_{\text{trap}}}{\eta} \int_0^\infty \rho_{NN}(t)\,t\,dt = \frac{\Gamma_{\text{trap}}}{\eta}(\mathcal{L}_{\text{tot}}^{-2}\rho(0))_{\text{NN}}$$

Efficiency η vs. transfer time τ

To have high efficiency we need $\Gamma_{\rm fl}$ to be small

Then effect of $\Gamma_{\rm fl}$ on η and τ may be treated perturbatively
(J Cao and RJ Silbey, 2009)

- τ is independent of $\Gamma_{\rm fl}$ to leading order
- η to leading order given in terms of τ:

$$\eta \approx \frac{1}{1 + \Gamma_{\rm fl}\tau}$$

- Maximizing η is equivalent to minimizing τ, so wlog will focus on τ in the following

Classical Model (Förster, 1965)

- Want to model network dynamics with classical (incoherent) master equation, where particle jumps from site to site

$$\frac{dP_i}{dt} = \sum_j (T_{j\to i} P_j - T_{i\to j} P_i)$$

- Need to match quantum behavior for fast dephasing rate γ:

$$(T_{\rm cl})_{i\to j} = \frac{2\Omega^2\gamma}{\gamma^2 + (\omega_i - \omega_j)^2}$$

for sites i, j, coupled by quantum hopping amplitude Ω

- For open system, adding escape rate is trivial, e.g. for linear chain

$$\frac{dP_i}{dt} = \frac{2\Omega^2\gamma\,(P_{i+1} - P_i)}{\gamma^2 + (\omega_{i+1} - \omega_i)^2} + \frac{2\Omega^2\gamma\,(P_{i-1} - P_i)}{\gamma^2 + (\omega_{i-1} - \omega_i)^2} - (\Gamma_{\rm fl} + \Gamma_{\rm trap}\delta_{i,N})P_i$$

Leegwater Approximation (Leegwater, 1996)

Leegwater approximation also takes form of a “classical” master equation but the rates are non-classical:

$$(T_{\mathrm{L}})_{i\to j} = \begin{cases} \frac{2\Omega^2\gamma}{(\gamma+\Gamma_{\mathrm{trap}}/2)^2+(\omega_i-\omega_j)^2}\,, \text{either } i \text{ or } j \text{ connected to trap} \\ \frac{2\Omega^2\gamma}{\gamma^2+(\omega_i-\omega_j)^2}\,, \quad \text{otherwise} \end{cases}$$

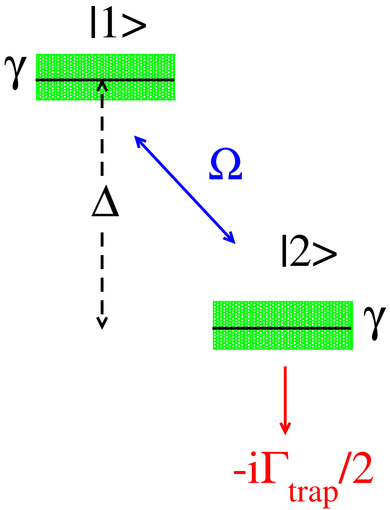
- Leegwater incorporates some effects of quantum coherence, e.g. resonance trapping
- In some important cases may provide useful approximation for quantum behavior even where classical model fails

Opening-Assisted Quantum Transport Enhancement

Begin with 2-site model incorporating

- Disorder (detuning)
- Dephasing
- Openness

Interested in time to reach trap starting from site 1

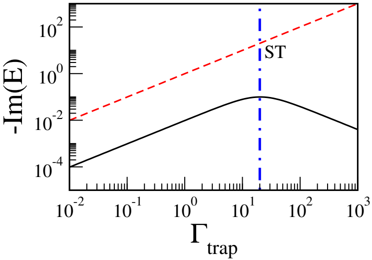


2-Site Model

Superradiance (SR) in 2-Site Model

Reorganization of resonance widths at $\Gamma_{\rm trap} = 2\Delta$

$\Omega = 1,\ \Delta = 10$

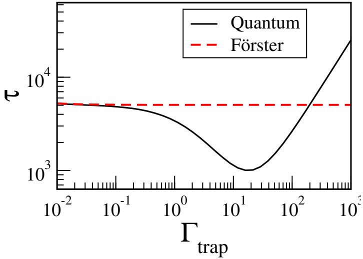


Opening-Assisted Quantum Transport

Quantum transport faster than classical
Transport optimized at SR transition

$\Omega = 0.1,\ \gamma = 1,\ \Delta = 10$

- Semiclassical regime – dephasing much faster than transport
- Nevertheless classical model breaks down at nonzero opening



2-Site Model

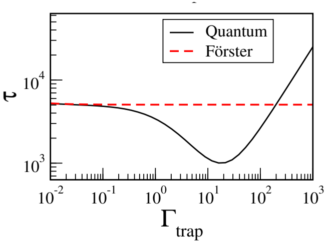
Analytic: Classical

$$\tau_{\mathrm{cl}} = \frac{1}{2\Omega^2}\left(\frac{4\Omega^2}{\Gamma_{\mathrm{trap}}} + \gamma + \frac{\Delta^2}{\gamma}\right)$$

Analytic: Quantum (=Leegwater!)

$$\tau_{\mathrm{Q}} = \tau_{\mathrm{L}} = \frac{1}{2\Omega^2}\left(\frac{4\Omega^2}{\Gamma_{\mathrm{trap}}} + \gamma + \frac{\Gamma_{\mathrm{trap}}}{2} + \frac{\Delta^2}{\gamma + \frac{\Gamma_{\mathrm{trap}}}{2}}\right)$$

Known result - e.g. J Cao & RJ Silbey, 2009

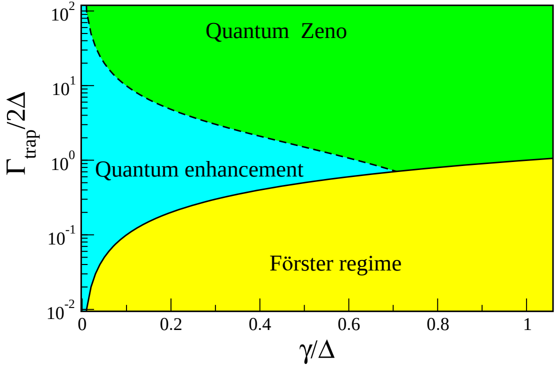


Observations:

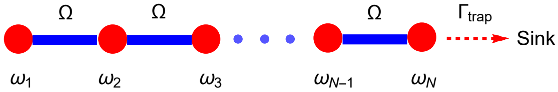
- For small Ω, optimal coupling to opening is $\Gamma_{\mathrm{trap}}^{\mathrm{opt}} = 2\Delta - 2\gamma$
- Quantum faster by factor $(\Delta^2 + \gamma^2)/2\Delta\gamma \approx \Delta/2\gamma$ for $\Delta \gg \gamma$
- Dephasing and openness combine to aid transport (counteracting localization)

Quantum Enhancement Regime in 2-Site Model

- Large opening $\Gamma_{\mathrm{trap}} \Rightarrow$ quantum suppression (Zeno / Resonance trapping)
- Small opening $\Gamma_{\mathrm{trap}} \Rightarrow$ classical Förster regime
- Quantum enhancement for Γ_{trap} near SR
- Enhancement regime grows with increasing disorder



What About Chain of Arbitrary Length N?



Need to average over disorder

$$\omega_i \in [-W/2, W/2] \quad \Rightarrow \quad \Delta^2 \to W^2/6$$

Analytic results:

$$\langle \tau_{\text{cl}} \rangle_W = \frac{N}{\Gamma_{\text{trap}}} + \frac{N(N-1)}{4\Omega^2}\left(\gamma + \frac{W^2}{6\gamma}\right)$$

$$\langle \tau_{\text{L}} \rangle_W = \frac{N}{\Gamma_{\text{trap}}} + \frac{N(N-1)}{4\Omega^2}\left[\gamma + \frac{\Gamma_{\text{trap}}}{N} + \frac{W^2}{6\gamma}\left(1 - \frac{2\Gamma_{\text{trap}}}{N(2\gamma + \Gamma_{\text{trap}})}\right)\right]$$

What About Chain of Arbitrary Length N?

Analytic results:

$$\langle \tau_{\mathsf{cl}} \rangle_W = \frac{N}{\Gamma_{\mathsf{trap}}} + \frac{N\,(N-1)}{4\Omega^2}\left(\gamma + \frac{W^2}{6\gamma}\right)$$

$$\langle \tau_{\mathsf{L}} \rangle_W = \frac{N}{\Gamma_{\mathsf{trap}}} + \frac{N\,(N-1)}{4\Omega^2}\left[\gamma + \frac{\Gamma_{\mathrm{trap}}}{N} + \frac{W^2}{6\gamma}\left(1 - \frac{2\Gamma_{\mathrm{trap}}}{N(2\gamma+\Gamma_{\mathrm{trap}})}\right)\right]$$

$$\frac{\langle \tau_{\mathsf{Q}} \rangle_W}{\langle \tau_{\mathsf{L}} \rangle_W} = 1 - O\left(\frac{\Omega^2}{\gamma W}\right)$$

For simplicity, take N large

Significant quantum enhancement over classical transport when:

$$\gamma \lesssim \frac{\Gamma_{\rm trap}}{2} < \frac{W^2}{6\gamma} - \gamma$$

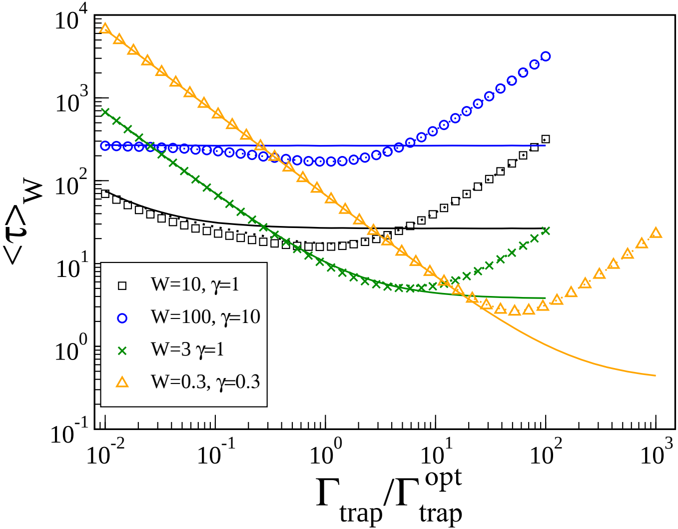
Again, need disorder sufficiently strong relative to dephasing

Optimal quantum transport for opening strength:

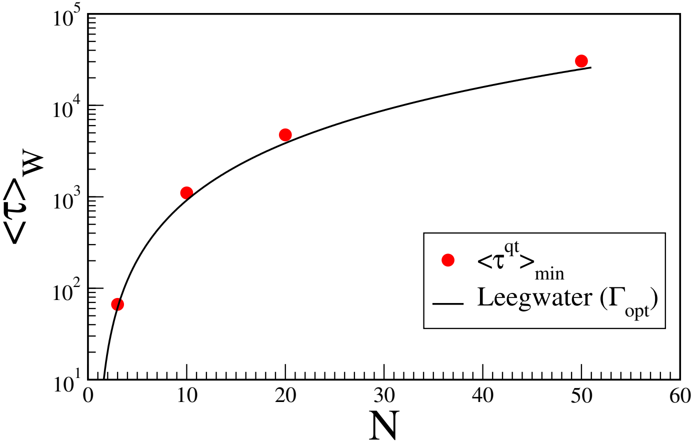
$$\Gamma_{\rm opt} = 2\left(W/\sqrt{6} - \gamma\right)$$

Note both results independent of chain length N!

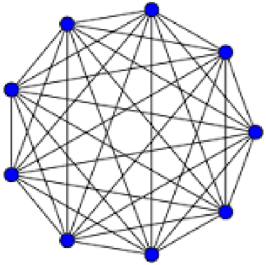
Linear Chain: Numerical Results ($N = 3$, $\Omega = 1$)



Linear Chain: Numerical Results ($\Omega = 1$, $\gamma = 10$, $W = 50$)



Fully Connected Network



$$\mathrm{H_{fc}} = \sum_{j=1}^{N} \omega_j \left| j \right\rangle \left\langle j \right| + \Omega \sum_{1 \le j < k \le N} \left(\left| j \right\rangle \left\langle k \right| + \left| k \right\rangle \left\langle j \right| \right)$$

As before, we

- Connect site N to opening with coupling $\Gamma_{\rm trap}$
- Start on (arbitrarily chosen) site 1
- Calculate average time τ to reach opening

Fully Connected Network: Calculations

Focus on regime of strong disorder and opening, where quantum transport enhancement is strongest

$$\Gamma_{\rm trap}/N \sim W/N \gg \gamma \gg \Omega$$

Quantum transport

$$\langle \tau_{\rm L} \rangle_W = \frac{3\Gamma_{\rm trap}^2 + 2W^2}{12\Omega^2\Gamma_{\rm trap}}$$

$$\frac{\langle \tau_{\rm Q} \rangle_W}{\langle \tau_{\rm L} \rangle_W} = 1 + O\left(\frac{N^2\Omega^2}{W^{3/2}\gamma^{1/2}}\right)$$

Classical transport

$$\langle \tau_{\rm cl} \rangle_W \sim \frac{W^2}{N\gamma\Omega^2} \qquad \text{(Levy Flight)}$$

Fully Connected Network: Calculations

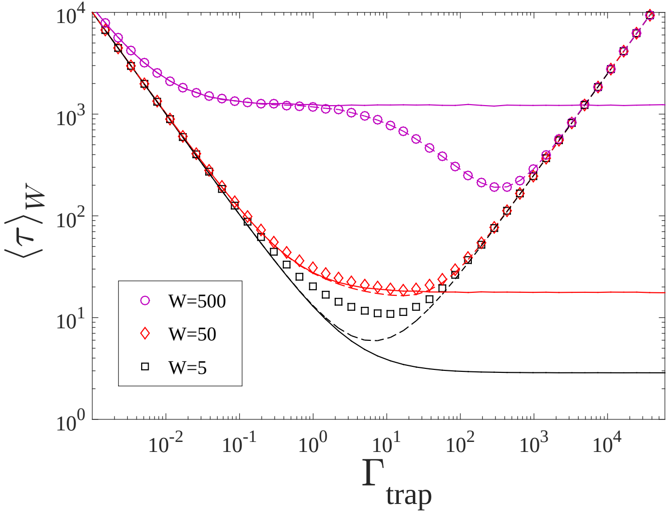
Optimal opening is again proportional to disorder

$$\Gamma_{\rm opt} = \sqrt{\frac{2}{3}} W$$

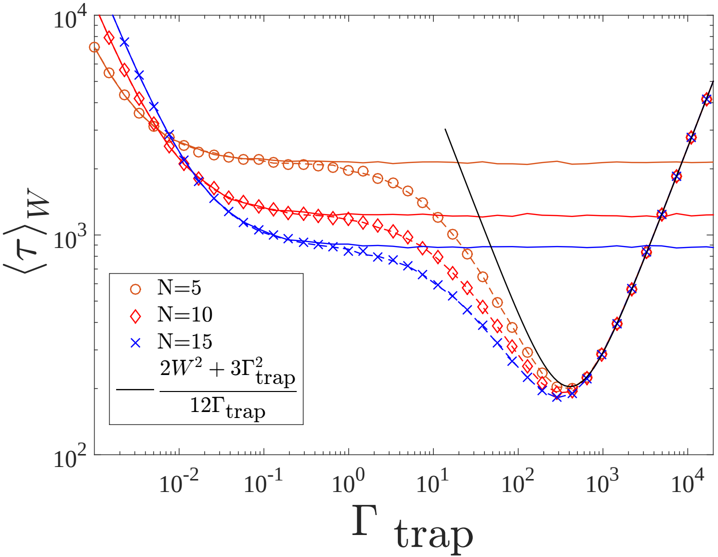
Quantum transport enhancement at optimal opening

$$\frac{\langle \tau_{\rm Q} \rangle_W}{\langle \tau_{\rm cl} \rangle_W} \sim \frac{\gamma}{W/N} \ll 1$$

Fully Connected Network ($N = 10$, $\Omega = 1$, $\gamma = 5$)



Fully Connected Network ($\Omega = 1$, $\gamma = 5$, $W = 500$)

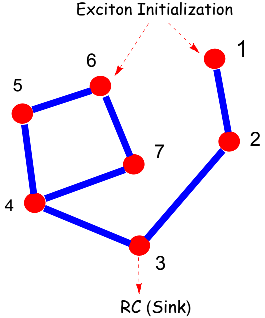


FMO Photosynthetic Complex

Each FMO subunit contains seven chromophores

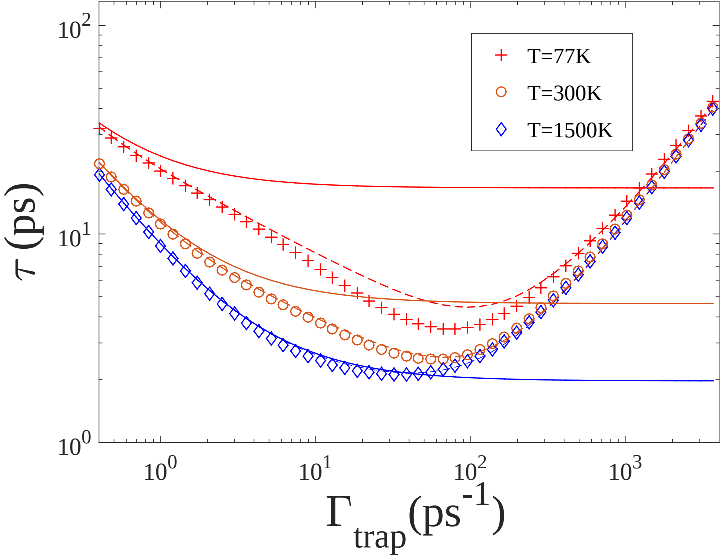
Connectivity intermediate between 1D chain and fully connected extremes

Dephasing rate $\gamma = 0.52(T/\mathrm{K})\ \mathrm{cm}^{-1}$ (Panitchayangkoon et al., 2010)



$$\mathrm{H}_{\mathrm{FMO}} = \begin{pmatrix} 200 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\ -87.7 & 320 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\ 5.5 & 30.8 & 0 & -53.5 & -2.2 & -9.6 & 6 \\ -5.9 & 8.2 & -53.5 & 110 & -70.7 & -17 & -63.3 \\ 6.7 & 0.7 & -2.2 & -70.7 & 270 & 81.1 & -1.3 \\ -13.7 & 11.8 & -9.6 & -17 & 81.1 & 420 & 39.7 \\ -9.9 & 4.3 & 6 & -63.3 & -1.3 & 39.7 & 230 \end{pmatrix} \mathrm{cm}^{-1}$$

FMO: Numerics



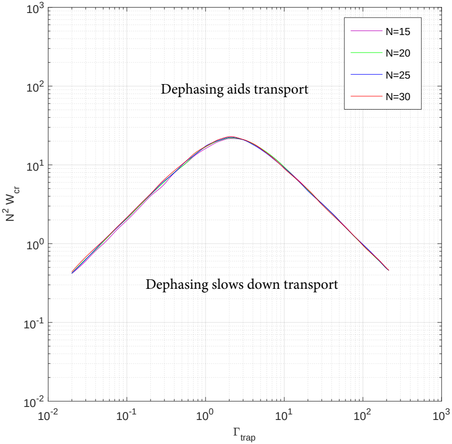
When Does Dephasing Aid Transport in Open Systems?

Answer: In linear chain, dephasing helps for disorder strength

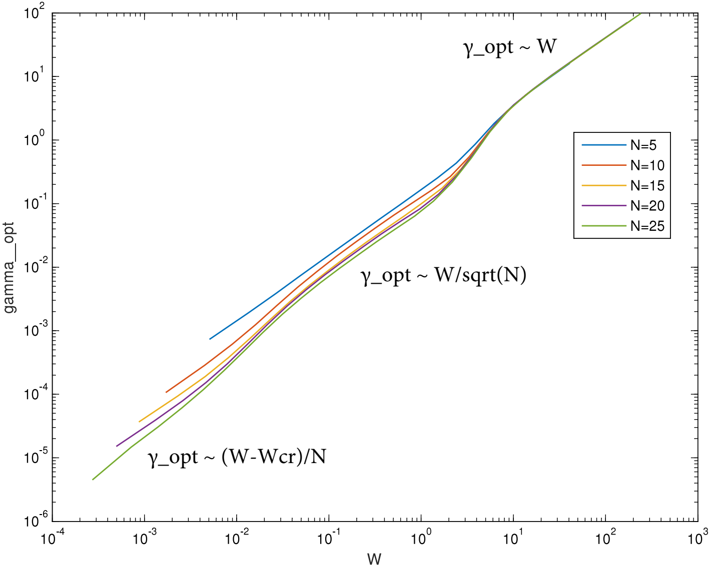
$$W > W_{\rm cr} \approx \min(\Gamma_{\rm trap}, \Omega^2/\Gamma_{\rm trap})/N^2$$

Notice strong (and non-monotonic) dependence on degree of opening!

$$\Omega = 1$$



Optimal Dephasing: Three Regimes ($\Omega = 1$, $\Gamma_{\text{trap}} = 1/16$)



Summary

- Non-Hermitian Hamiltonian formalism is general framework for studying open quantum systems with disorder and dephasing
- Quantum systems display non-trivial behavior as opening size varied: strongly enhanced coherent transport near superradiance transition
- Effect survives at finite temperature if temperature not too high (compared to energy scales in Hamiltonian)
- Analytic results obtained in paradigmatic models: Linear chain, fully connected network
- FMO is example of opening-assisted coherent transport enhancement
- Regime of noise-assisted transport also depends strongly on degree of opening

Thank you!