Dynamical role of quantum coherence and environment in multichromophoric energy transfer

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Quantum coherence in photosynthetic complexes

- G. Engel et al., Nature (07).
- E. Collini, G. Scholes, Science (09).

- How to explore dynamical interplay between quantum coherence and environment
- How to quantify their contributions to energy transfer efficiency

PHOTONS

ANTENNA PIGMENTS
(Chlorophyll molecules and other pigments)

energy transfer

REACTION CENTER

Fenna-Matthews-Olson (FMO) Complex
Can we partition dynamics of open quantum systems into contributions associated with fundamental physical mechanisms?
Multichromophoric Energy transfer

A set of multichromophores which guides excitation energy between two points A and B.

Free Hamiltonian for M chromophores is:

\[ H_S = \sum_{m=1}^{M} \varepsilon_m a_m^\dagger a_m + \sum_{m<n} V_{mn} (a_m^\dagger a_n + a_n^\dagger a_m) \]

System-Bath Hamiltonians:

Thermal phonon bath

\[ H_p = \sum_m q_m a_m^\dagger a_m \]

Radiation field

\[ H_r = \sum_m q_m^r (a_m + a_m^\dagger) \]
Lindblad master equation for multichromophoric systems

Master Equation (Born-Markov and secular approximations):

\[
\frac{\partial \rho(t)}{\partial t} = -i [H_S + H_{LS}, \rho(t)] + L_\rho \rho(t) + L_r \rho(t)
\]

Lindblad superoperator:

\[
L_k \{ \rho(t) \} = \sum_{\omega} \sum_{m,n} \gamma_{mn}^k (\omega) [A_m^k (\omega) \rho A_n^{k\dagger} (\omega) - \frac{1}{2} A_m^k (\omega) A_n^{k\dagger} (\omega) \rho - \frac{1}{2} \rho A_m^k (\omega) A_n^{k\dagger} (\omega)]
\]

\[
\gamma_{mn} (\omega) = C_{mn} \int dt e^{i\omega t} \langle q_m(t) q_n(0) \rangle
\]

Lindblad operators

\[
A_m (\omega_{MN}) = c_m^* (N) c_m (M) |M\rangle \langle N|
\]

\[
\gamma(\omega) = 2\pi [J(\omega)(1 + n(\omega)) + J(-\omega)n(-\omega)]
\]

where \( n(\omega) = \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1} \)

Reorganization energy

Bath spectral density:

\[
J(\omega) = \frac{E_R}{\hbar \omega_c} \frac{1}{\omega_c} \exp\left(-\frac{\omega}{\omega_c}\right)
\]
Directed quantum walks in excitation manifolds

\[ |00\cdots0\rangle \]

Directed quantum walk

Quantum jumps in a fixed excitation manifold

Damped evolution

\[ \frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H_{\text{eff}}, \rho(t)]^* + \sum \Gamma_{m,m',n,n'} W_{m,m'} \rho W_{n,n'}^\dagger + \sum \gamma_m R_m \rho R_m^\dagger \]

Quantum jumps to \( j+1 \) or \( j-1 \) exciton manifold

Probability of a jump:

\[ \sum_{m=1} \gamma_m \text{Tr}[R_m \rho R_m^\dagger] dt \]


A. Olaya-Castro, et. al, Phys. Rev. B (08)
Directed quantum walks

\[
H_{\text{eff}} = H_S + H_{LS} + H_{\text{decoher}}
\]

\[
H_{\text{decoher}} = -\frac{i}{2} \left[ \sum_{m} \Theta_{m,n}^p a_m^\dagger a_n + \sum_{m} \sum_{\omega} \gamma_{m}^r (\omega) a_m^\dagger a_m + H_{\text{trap}} \right]
\]

Classical Random Walk:
\[
\frac{dp_a(t)}{dt} = \sum_b M_{ab} p_b(t)
\]

Directed Quantum Walk:
\[
\frac{d\rho_a(t)}{dt} = \sum_b M_{ab} \rho_b(t)
\]

\[
M_{ab} = -\frac{i}{\hbar} (I \otimes H_{\text{eff}} - H_{\text{eff}}^* \otimes I) + \sum_{m,m',n,n'} \Gamma_{m,m',n,n'}^p (W_{n,n'}^* \otimes W_{m,m'}_{ab})
\]
The energy transfer efficiency of the channel is defined as the integrated probability of the excitation successfully being trapped:

\[ \eta = \int_0^\infty \text{Tr}[H_{\text{trap}} \rho(t)] dt \]

The energy transfer time:

\[ \tau = \int_0^\infty t \text{Tr}[H_{\text{trap}} \rho(t)] dt \]
Environment-assisted quantum walks

Why improvement is helpful? [Easy]
How to quantify the role of coherence/environment. [Not so easy]

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Why is environment helpful?

"Funnel"

1

6

3

Energy basis

Site basis

Barrier

1

3

"Energy basis" and "Site basis" concepts are illustrated in a diagram, showing the relationship between barrier and efficiency as a function of reorganization (cm⁻¹). The graph depicts efficiency increasing with reorganization, highlighting the role of the environment in facilitating these processes.

Illustrations of "Funnel" and barrier structures are shown, with numbers 1, 3, and 6 indicating points of interest or stages in the process.
Master equation (schematically)

\[
\frac{d}{dt} \rho(t) = \begin{cases} \text{Coherent} & + E_R \\ \text{Relaxation} & + E_R \\ \text{Dephasing} & \end{cases} + \frac{i}{\hbar}[H_S, \rho(t)] \\
+ \begin{cases} \text{Recombination} & + H_{\text{recomb}} \\ \text{Trapping} & + H_{\text{trap}} \end{cases}
\]
Partitioning Energy Transfer Efficiency

Master equation

\[ \frac{\partial}{\partial t} \rho(t) = \mathcal{M} \rho(t) \]

Efficiency

\[ \eta = \frac{2}{\hbar} \int_{0}^{\infty} \text{Tr}\{H_{\text{trap}} \rho(t)\} dt \]

Superoperator

\[ \mathcal{M} = \sum_{k} \mathcal{M}_{k} \]

Contributions to efficiency

\[ \eta = \sum_{k} \eta_{k} \]

For example

\[ \text{What is the contribution of coherent evolution?} \]
Contributions to ETE

\[ M = L + H_{\text{ref}} \quad ; \quad L = \sum_k L_k \]

Identity for Green’s function

\[ M^{-1} = H_{\text{ref}}^{-1} + H_{\text{ref}}^{-1} \sum_k L_k M^{-1} \]

\[ L_k = \begin{cases} \text{Coherent} & , \\ \text{Recombination} & \end{cases} \]

\[ H_{\text{ref}} = \begin{cases} \text{Relaxation} & , \\ \text{Dephasing} & \end{cases} \]

Similar in spirit to
Contributions to ETE

\[ \eta = \sum_{k} \eta_k \]

Simplify efficiency

\[ \eta = -\frac{2}{\hbar} \text{Tr} \left\{ H_{\text{trap}} M^{-1} \rho(0) \right\} \]

\[ \eta_k = -\frac{2}{\hbar} \text{Tr} \left\{ H_{\text{ref}}^{-1} L_k M^{-1} \rho(0) \right\} \]
Contributions to ETE

- Crossover from quantum to relaxation regime
- Quantum coherent contribution ~10%

\[ \eta = \sum_k \eta_k \]


\( T = 300\text{K} \)
\( E_R = 35\text{cm}^{-1} \)
Spatially Correlated Bath

\[ \langle q_m(t) q_n(0) \rangle = C_{mn} \langle q(t) q(0) \rangle ; \quad C_{mn} = e^{-R_{mn}/R_c} \]

\[ \begin{align*}
\delta_{mn} & \quad \quad R_c \to 0 \\
1 & \quad \quad R_c \to \infty
\end{align*} \]

Efficiency versus Correlation radius [nm]

- Relaxation
- Coherent
- Dephasing
The effects of static disorder

- Relaxation
- Coherent
- Dephasing

Graphs showing efficiency versus reorganization energy, acceptor rate, and temperature.
Nonlocal dynamical contributions to ETE

\[ \rho(t) = F(t,0)\rho(0) \]

\[ M = \sum_k M_k \]

\[ M_k \rightarrow \lambda_k M_k \]

\[ \frac{\partial \rho(t)}{\partial t} = M\rho(t) \quad \rightarrow \quad \frac{\partial \rho(t)}{\partial t} = \sum_k \frac{1}{\hbar} \int_0^t F(t,t')M_k F(t',0)\bar{\rho}(0)dt' \]

\[ \eta_{k_{\pm}} = \frac{2}{\hbar} \int_0^\infty dt \int_0^t dt' \frac{1}{t'} \frac{1}{\partial \lambda_{k_{\pm}}} Tr\{H_{trap}\rho(t)\} \]
Comparison

Green function’s method

Energy transfer susceptibilities
Spatial Pathways
Conclusion & Outlook

- Environmental interactions lead to high energy transfer efficiency for the FMO complex
- Contribution measure reveals underlying dynamics
- FMO complex: Relaxation is dominant effects ~80%, quantum coherence ~10%

- Generalization to non-Markovian dynamics and strong bath
- Quantifying the limitations of quantum transport in open systems
- Optimizing charge and energy transfer
Applications

- How can we improve quantum state transfer in noisy and disordered networks?

- Can we enhance charge and energy transfer in biological systems and nano-devices using quantum interference?

- Can we engineer artificial materials to achieve optimal energy transport in realistic environments by exploiting quantum effects?
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