Photosynthetic Light Harvesting and Electronic Quantum Coherence Effects

Yuan-Chung Cheng
yuanchung@ntu.edu.tw

Department of Chemistry
National Taiwan University

NTHU Physics, December 5, 2010
Outline

• Photosynthetic light harvesting systems
• Experimental evidences for quantum coherence effects in photosynthesis
• Theoretical modeling of quantum dynamics & nonlinear spectroscopy of light harvesting complexes
• Coherent dynamics in the FMO complex: coherence assisted excitation energy transfer mechanism
• Concluding remarks
• Might be the most important photochemical process on earth
• Still, there is much unknown and much to be learned & modeled after
• Collecting sun-light energy with high efficiency is not trivial

\[6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{hv} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2\]
Light Harvesting in Photosynthesis

The “light” reactions

Blue-absorbing pigments

Orange-absorbing pigments

Red-absorbing pigments

Reaction Center

Light-harvesting complexes

…Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of NADP^+, ATP synthesis…
Primary Processes of Photosynthesis

Light harvesting in the antenna & charge separation in the reaction center ➔ remarkable, near unity quantum yield

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Light-harvesting Apparatus of Purple Bacteria

AFM of native photosynthetic membranes of a purple bacterium

Light-harvesting Apparatus of Higher Plants

(Bassi group)
Photosystem I Supercomplex of Plants

Chlorophyll Arrangement in the PS I Core

“A paradigmatic scenario of transport phenomena in a nanoscale network”

- electronic couplings & excitons
- complex network
- static & dynamical disorder
- “wet & warm” protein environments
- quantum coherence

PS I Core complex
96 Chls

Pdb id: 1JB0

A complex chlorophyll network for light harvesting
New Insights into Photosynthetic Light Harvesting

• Recent experiments indicate that quantum coherence can play a role in light harvesting


New Insights into Photosynthetic Light Harvesting

- Recent experiments indicate that quantum coherence can play a role in light harvesting – **even at ambient temperature**


Quantum Coherence in FMO at Physiological Temperature

http://arxiv.org/abs/1001.5108
Coherent Evolution of Density Matrix

- Time-evolution of a superposition of exciton states:
  \[ |\Psi(t)\rangle = ae^{-i\omega_1 t} |e_1\rangle + be^{-i\omega_2 t} |e_2\rangle \]
- Density matrix with *excitonic coherence*:
  \[ |\Psi(t)\rangle\langle\Psi(t)| = |a|^2 |e_1\rangle\langle e_1| + |b|^2 |e_2\rangle\langle e_2| + ab^* e^{-i(\omega_1 - \omega_2) t} |e_1\rangle\langle e_2| + a^* b e^{i(\omega_1 - \omega_2) t} |e_2\rangle\langle e_1| \]
- Coherence oscillation results in energy population moving reversibly among multiple chromophores.
- Coherence dynamics can be probed by using 2-D photon echo spectroscopy: quantum beats in 2-D signals.
How does such long-lasting electronic coherence affect light harvesting?

Combine experimental results & theoretical modeling to find out!
Strategy for Theoretical Investigations

• In order to elucidate how quantum coherence affects excitation energy transfer in the FMO complex, we
  – Build an effective model for FMO excitations & dynamics of excitation energy transfer
  – Refine the theoretical model by comparing to experimental two-dimensional optical spectra
  – Simulate the dynamics of energy trapping both with and without quantum coherence
  – Compare the results to determine the role of electronic quantum coherence
Light-harvesting Apparatus of Green Sulfur Bacteria

Fenna-Matthews-Olson Complex from Green Sulfur Bacteria

well characterized model

PDB ID: 4bcl, 1m50

Modeling Excitation Energy Transfer in the FMO?

Full quantum dynamics of such a system is infeasible!
Frenkel Exciton Model

$\varepsilon_1, \varepsilon_2$: site energy, transition energy modified by proteins
Exciton Hamiltonian and Excitonic Coupling

- Excitations interact with each other through excitonic coupling $J$
- $H_e \rightarrow$ transition energies and excitonic couplings in multichromophoric systems!!

\[
H_e = \begin{bmatrix}
\varepsilon_1 & J_{12} & \cdots & J_{1N} \\
J_{12} & \varepsilon_2 & \cdots & J_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
J_{1N} & J_{2N} & \cdots & \varepsilon_N
\end{bmatrix}
\]

“site basis”

- Excitation energy transfer induced by excitonic coupling $J$
FMO Complex: Electronic Interactions

- There is a good starting point for the model of FMO Hamiltonian
- Couplings from quantum chemistry + transition density cube calculations
- Site energies from fitting to optical spectra

Site energies

<table>
<thead>
<tr>
<th>Site</th>
<th>BChl</th>
<th>Monomer</th>
<th>Trimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12,445</td>
<td>12,410</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12,520</td>
<td>12,530</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12,205</td>
<td>12,210</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12,335</td>
<td>12,320</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12,490</td>
<td>12,480</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>12,640</td>
<td>12,630</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>12,450</td>
<td>12,440</td>
<td></td>
</tr>
</tbody>
</table>

Excitonic couplings

* For C. Tep. FMO, unit in cm$^{-1}$

Quantum Dynamics of Excitation Energy Transfer

When system-bath coupling is weak, we can use Redfield equation to describe energy transfer:

\[
\partial_t \rho(t) = -i[H_\text{e}, \rho(t)] - \mathcal{R}[\rho(t)]
\]

\[
\rho = \begin{bmatrix}
\rho_{11} & \rho_{12} & \cdots & \rho_{1N} \\
\rho_{12} & \rho_{22} & \cdots & \rho_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
\rho_{1N} & \rho_{2N} & \cdots & \rho_{NN}
\end{bmatrix}
\]

\(\rho\): reduced-system density matrix

N: number of chromophores

\[\mathcal{R}[]: \rho_{nn} \rightarrow \rho_{mm}: \text{population dynamics (incoherent)}\]

\[\rho_{nm} \rightarrow \rho_{n'm'}: \text{coherence dynamics}\]
Calculate Nonlinear Spectrum

Also consider light-matter interactions with laser pulses to simulate nonlinear spectrum using dynamical propagation

\[
\partial_t \rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \mathcal{R}[\rho(t)]
\]

- exciton Hamiltonian
- dissipation
- light-matter interactions

\[
H_{\text{int}}(t) = -\hat{V} \cdot \sum_{a=1}^{3} E_a(t)
\]

- Extract photon-echo signal at the phase-matching direction by selective combinations of light-matter interactions in calculations (non-trivial)

M. F. Gelin, D. Egorova, W. Domcke, JCP 123, 164112 (2005);
QDAS Code

- Quantum Dynamics And Spectroscopy
- Simulates excitation energy transfer dynamics and various linear & nonlinear spectra (Absorption, 2D, 3PEPS…)
- Treats an array of bath spectra densities and bath memory effects
- Includes doubly excited states and average over a Gaussian distribution of disordered energies
- MPI capability for parallel computing
Renger’s model does not provide adequate 2D electronic spectra

Parallel computing is necessary for seeking a better model:

- each spectrum needs ~ 12 hrs using 128 CPUs on NERSC’ Franklin cluster due to extensive Monte-Carlo ensemble averaging procedure
- > 30 parameters to adjust/optimize
• Iterate to reach good agreement between experiment & theory starting from Renger’s model
• Require inclusion of doubly excited states and average over a Gaussian distribution of disordered energies
• Provide refined model ➔ basis for studying coherence effects
Coherent vs. Incoherent Model

- Use the refined theoretical model to investigate the effects of quantum coherence on excitation energy transfer
- Two theories for energy transfer dynamics:
  - Coherent: full quantum master equation
  - Incoherent: population dynamics only ➔ conventional excitation hopping view
- Initial conditions: coherent superposition for the coherent picture, and population-only for the incoherent picture
coherent picture

incoherent picture

0000 fs

site population
Dynamics in the Site Basis

Coherent Picture

Incoherent Picture

- Reversible population redistribution in space showing interference effects due to quantum coherence
- Efficiencies of reaching BCHl 3 only marginally different.
Energy Trapping from BChl 3

FMO complex is a energy wire connected to RC through BChl 3

What if an efficient energy trap is attached to BChl 3?
- Rapid trapping (50 fs) from BChl 3 enhances efficiency for the coherent case because of the suppression of back transfer.
- Quantum coherence may enable excitation to find RC rapidly through reversible sampling in space ➔ *Coherence assisted energy trapping*
Coherence Assisted Energy Trapping

- Long-lived electronic coherence enables the system to perform rapid and reversible sampling in space to search for the trap site
- Efficient trapping process dissipates the energy and localizes the excitation
- The scheme can be more efficient than incoherent hopping and is likely to be more robust on energetically disordered landscape
- This proposal is currently being actively studied by many groups: Aspuru-Guzik (Harvard), Lloyd (MIT), Whaley (Berkeley), Plenio (Imperial College, UK)…
How is the long-lasting quantum coherence achieved?

1. Protein environment & correlated motions
2. Non-equilibrium effects in energy transfer
Coherence Photon Echo of Bacterial Reaction Center

• Protein protection of electronic quantum coherence:
The Reaction Center of Purple Bacteria

BChlB (B_B)  BChlA (B_A)
BPhyB (H_B)  BPhyA (H_A)
UQ_B   Fe   UQ_A
The Reaction Center of Purple Bacteria

- BChl$_B$ (B$_B$)
- BPhy$_B$ (H$_B$)
- UQ$_B$
- BChl$_A$ (B$_A$)
- BPhy$_A$ (H$_A$)
- UQ$_A$
- Fe
Probing H/B Coherence Dynamics:
Two-color Electronic Coherence Photon Echo

- |H⟩ and |B⟩ selectively excited
- Design to probe coherence specifically |g⟩⟨H| in t₁, |B⟩⟨H| in t₂

Ordering: 750-800-750 (nm)

|g⟩⟨g|  |g⟩⟨H|  |B⟩⟨H|  signal
Experimental Data @ 77K

Photon-echo Intensity
Mapping Coherence Dynamics in the RC

- Photon-echo intensity measured in this two-color experiment follows coherence dynamics.
- Along $t_1$: $|g\rangle\langle H|$ dephasing
- Along $t_2$: $|B\rangle\langle H|$ dephasing

Dephasing of Electronic Coherence

• Phase associated with the time evolution of coherences (off-diagonal density matrix elements):

\[ \phi_{ij}(t) = e^{-i(w_i-w_j)t} \]

⇒ Randomness in the energy gap \( \delta \omega_{ij}(t) \) results in dephasing

⇒ Fluctuations of the energy gap are induced by dynamics of the protein environment

• Stronger fluctuation ⇒ faster dephasing
Mapping Coherence Dynamics

- Rapid \(|g\rangle\langle H|\) dephasing \((t_1)\)

\[ |B\rangle \langle H| \text{ dephasing} \]

Photon-echo Intensity

\[ |g\rangle \langle H| \text{ dephasing} \quad \rightarrow \quad \text{Large } E_H \text{ fluctuations.} \]

Mapping Coherence Dynamics

- Slow $|B\rangle\langle H|$ dephasing ($t_2$)

$|g\rangle\langle H|$ dephasing

$\Rightarrow$ Smaller $E_H - E_B$ energy gap fluctuations.

Mapping Coherence Dynamics

- Rapid $|g\rangle\langle H| \text{ dephasing (} t_1 \rangle$ → Large $E_H$ fluctuations.
- Slow $|B\rangle\langle H| \text{ dephasing (} t_2 \rangle$ → Smaller $E_H-E_B$ energy gap fluctuations.
- Energy fluctuations on B and H are highly correlated.
- Evidence for correlated protein environments!

### Theoretical Modeling

<table>
<thead>
<tr>
<th>State</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g\rangle\langle g)</td>
<td>Impulsive response function formalism. BPhy-BChl electronic coupling (\sim 220 \text{ cm}^{-1}). Transition energy fluctuations on Bphy/BChl:</td>
</tr>
<tr>
<td>(B\rangle\langle g)</td>
<td>(C_{BPhy}(t) = \lambda_{BPhy} \exp(-t^2 / \tau_0^2) + \Delta_0^2),</td>
</tr>
<tr>
<td>(B\rangle\langle H)</td>
<td>(C_{BChl}(t) = \lambda_{BChl} \exp(-t^2 / \tau_0^2) + \Delta_0^2).</td>
</tr>
<tr>
<td>(g\rangle\langle H)</td>
<td>Cross-correlation between BPhy and BChl fluctuations (described by (c)):</td>
</tr>
<tr>
<td>(g\rangle\langle g)</td>
<td>(C_{hb}(t) = \lambda_{hb} \exp(-t^2 / \tau_0^2) + \Delta_0^2; \lambda_{hb} = c\sqrt{\lambda_h\lambda_b}).</td>
</tr>
</tbody>
</table>

250 cm\(^{-1}\) vibrational mode coupled to BPhy (sawtooth pattern).
Experiment vs. Theory

Protein Protection of Electronic Coherence

- Electronic coupling alone ($c=0.6$) cannot explain the long dephasing time.
- Strong cross-correlations ($c\sim0.9$) between protein environments responsible for long-lived $|B\rangle\langle H|$ coherence.

$|B\rangle\langle H|$ dephasing times: $t_{g,77K}=440\text{fs}$, $t_{g,180K}=310\text{fs}$
Non-equilibrium Effects in Excitation Energy transfer

- Non-equilibrium effects could be important in ultrafast dynamics
- Conventional theories assume that baths are always in equilibrium → over-estimate of coherence dephasing rate!

**Photon-induced dynamics**

**Redfield/Forster picture**

![Diagram](image-url)
Non-equilibrium Effects Lead to Longer Decoherence Time

- Calculations based on new theoretical formalism including non-equilibrium bath effects show longer decoherence time
- New theory predicts quantum coherence lasting in the FMO complex at physiological temperature (Ishizaki & Fleming, PNAS 2000)

Concluding Remarks

- Energy transfer through quantum coherence has been revealed in photosynthesis
- Coherent dynamics may promote energy trapping in light harvesting
- Correlations in protein dynamics & non-equilibrium bath effects contribute to the preservation of coherence
- High-performance computing crucial for studies of quantum dynamics, spectra, molecular quantum chemistry, protein dynamics, complex organization …etc.
Acknowledgements

• Graham Fleming (UC Berkeley)
• Seogjoo Jang (Queens College, CUNY)
• The Fleming Group (UC Berkeley)

• National Science Council of Taiwan
Thank You!
We use a time-nonlocal approach to retain memory effects:

\[
\frac{d}{dt} \rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \int_0^t K(t, \tau) \rho(\tau) d\tau
\]

• Important for the description of peak shape
• \(K(t, \tau)\) memory kernel, can be calculated from \(\Omega(\omega)\) using perturbation theory
• Decompose \(K(t, \tau)\) into exponentials to facilitate efficient propagation of time-nonlocal dynamics

Propagating Dynamics with Bath Memory

• Redfield theory ➔ does not describe full \( \langle \delta \omega(t) \delta \omega(0) \rangle \)

\[
\frac{d}{dt} \rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \mathcal{R}(t) \cdot \rho(t)
\]

• We use a time-nonlocal approach to retain memory effects:

\[
\frac{d}{dt} \rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \int_0^t K(t, \tau) \rho(\tau) d\tau
\]

• \( K(t, \tau) \) ➔ memory kernel, can be calculated from \( C(t) \) using perturbation theory

Theoretical Background

Photosynthetic Excitons & Quantum Dynamics
Exciton Hamiltonian and Excitonic Coupling

- Excitations interact with each other through excitonic coupling $J$
- $H_e \rightarrow$ transition energies and excitonic couplings in multichromophoric systems!

\[
H_e = \begin{bmatrix}
\varepsilon_1 & J_{12} & \cdots & J_{1N} \\
J_{12} & \varepsilon_2 & \cdots & J_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
J_{1N} & J_{2N} & \cdots & \varepsilon_N
\end{bmatrix}
\]

“site basis”

- Excitation energy transfer induced by excitonic coupling $J$
- When $J$ is significant, the eigenstates of $H_e$ has to be considered $\rightarrow$ excitons
Excitonic Coupling and Photosynthetic Excitons

- Excitonic coupling $J$ can result in delocalized excitations $\rightarrow$ excitons
- Optical transitions correspond to excitonic transitions

$$H_e = \begin{bmatrix}
E_1 & 0 & \cdots & 0 \\
0 & E_2 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & E_N \\
\end{bmatrix}$$

“exciton basis”

|1⟩ excitons |2⟩

E1 E2

Normalized Absorption (a.u.)

700 750 800 850 900

Wavelength (nm)
Dynamics in the Condensed Phase

Energy of an individual chromophore $i$ modulated by its protein environment:

$\hbar \omega_{eg}^i(t) = \langle \omega_{eg} \rangle + \delta \omega_i(t) + \varepsilon_i$

$\delta \omega_i(t)$ → fast, dynamical changes
$\varepsilon_i$ → slow, static changes
$f(\varepsilon_i)$: inhomogeneous broadening
Modeling Excitation Energy Transfer: System-Bath Model

- Environments (baths) ➔ harmonic oscillators
- System-bath couplings ➔ correlation function:
  \[ C(t) = \langle \delta \omega(t) \delta \omega(0) \rangle \]
  or spectral densities:
  \[ \Omega(\omega) = \sum_{\alpha} \frac{c_\alpha^2}{2m_\alpha \omega_\alpha} \delta(\omega - \omega_\alpha) \]
- Reduced density matrix:
  \[ \rho = \sum_n P_n \ket{\psi_n} \bra{\psi_n} \]
  ➔ \( H_e \) and \( \Omega(\omega) \) determine the dynamics, \( \rho(t) \).
Redfield Picture of Excitation Energy Transfer

When system-bath coupling is weak, we can use Redfield equation to describe energy transfer:

\[
\partial_t \rho(t) = -i[H_e, \rho(t)] - \mathcal{R}[\rho(t)]
\]

\(\mathcal{R}[\rho(t)]\): population dynamics (incoherent)
\(\rho_{nn} \rightarrow \rho_{mm}\)

\(\mathcal{R}[\rho(t)]\): coherence dynamics
\(\rho_{nm} \rightarrow \rho_{n'm'}\)

\(\rho = \begin{bmatrix}
\rho_{11} & \rho_{12} & \cdots & \rho_{1N} \\
\rho_{12} & \rho_{22} & \cdots & \rho_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
\rho_{1N} & \rho_{2N} & \cdots & \rho_{NN}
\end{bmatrix}\)

\(N\): number of chromophores

\(\rho\): reduced-system density matrix
Sawtooth Pattern from Vibrational Coherence

Vibrational coherence induced by pulse 1 explains the sawtooth pattern:

A non-orthogonal cut ($t_1$) leads to the sawtooth pattern.
Two-dimensional Electronic Spectroscopy

\[ E_s(\tau, T, \omega_t) \sim iP^{(3)}(\tau, T, \omega_t) \]

Fourier transform along \(\tau\)

\[ E_s(\omega_\tau, T, \omega_t) \]

Energy transfer

\(\omega_\tau\) (input)

\(\omega_t\) (output)

spectrometer

sample

local oscillator (LO)
Electronic Coherence in FMO (77K)

- 2D electronic spectra show quantum beats on the diagonal cuts
- Strong evidence for long-lasting excitonic coherence (> 600 fs) in the Fenna-Matthews-Olson Complex ➔ coherent wavelike energy transfer
- True electronic quantum effect may play a role in energy transfer

Simple Model for Coherence Assisted Energy Trapping

Consider energy transfer within a dimer of two coherently coupled sites:

Bloch dynamics using 450 fs A/B dephasing time, 500 fs intrinsic A→B transfer time; actually modeled based on parameters suitable for a photosynthetic reaction center
Simple Model for Coherence Assisted Energy Trapping

Adding rapid trapping by \( T \) results in rapid \( A \) population decay ➔ only possible because of coherent oscillation

\[
\text{With } T
\]

\[
\begin{align*}
\text{site population} & \quad \text{time (fs)} \\
0 & \quad 200 \quad 400 \quad 600 \quad 800 \quad 1,000
\end{align*}
\]

\( T \) efficiently captures energy on \( B \) at the maxima!!

\[
\begin{align*}
450 \text{ fs } A/B \text{ dephasing time, } \quad 500 \text{ fs } A \rightarrow B \text{ transfer time, } \quad 50 \text{ fs } B \rightarrow T \text{ time.}
\end{align*}
\]
Simple Model for Coherence Assisted Energy Trapping

Quantum coherence promotes the efficiency of light capture

Coherent: reversible on A/B

Incoherent: station to station, A\rightarrow B transfer limiting the rate

This model explains efficient excitation energy trapping in the photosynthetic reaction center of purple bacteria

Lee, Cheng & Fleming, UP2008