

# On quantum models of excitation energy transfer in photosynthesis

Jesús Montejo-Gámez (in collaboration con J. L. López)



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# Motivation: Learning from Nature

- Experimental evidence of quantum coherence
  - G. Fleming et al. for the FMO complex at 77 K<sup>1</sup>
  - E. Collini et al. in cryptophyte algae at 180 K<sup>2</sup>
  - Reviews of Y.-C. Cheng and G. Fleming<sup>3</sup> and G. Scholes et al.<sup>4</sup>
- Highly efficient ET observed in higher plants<sup>5</sup>

CHALLENGES: Understanding the photosynthetic ET mechanism, developing mathematical models, designing artificial devices to improve our lives.

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<sup>1</sup> *Nature*, 446: 782-786, 2007

<sup>2</sup> *Nature*, 463: 644-648, 2010

<sup>3</sup> *Annu. Rev. Phys. Chem.* 60: 241-262, 2009

<sup>4</sup> *Nat. Chem.*, 23;3(10):763-774, 2011

<sup>5</sup> R.E.Blankenship, MOLECULAR MECHANISMS OF PHOTOSYNTHESIS, London:Blackwell Sci, 2002 ↻ 🔍

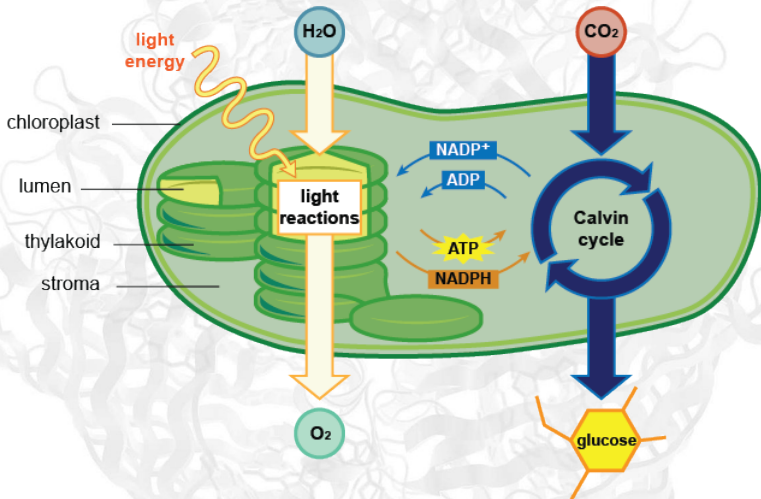
# Outline

- ① Excitation energy transfer in photosynthesis
- ② Mathematical formulation
- ③ Models of relevance
  - Förster theory
  - Redfield theory
- ④ 'Equilibrate' coupling regime
- ⑤ Prospects



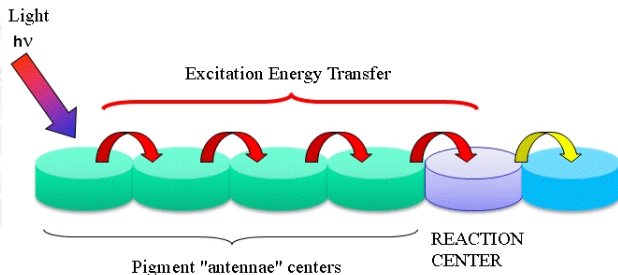
# Excitation energy transfer in photosynthesis

# Photosynthesis



# Excitation Energy Transfer

- Photosynthesis begins when light incides on the 'antennae' pigments, exciting them
- Each excited molecule transfers energy to others, so recovering its ground state
- In this way, the energy 'travels' to the reaction center



Along the transfer there are neither heat flux nor radiation.  
It is called EXCITATION ENERGY TRANSFER (EET)

# Purpose

- Developing a suitable formalism which allows to model the EET mechanism for the different photosynthetic complexes arising in Nature, as well as the factors which may take part in the energy migration.
- Showing the main models accounting for EET, their hypotheses and their applicability to real cases.

# Purpose

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# Mathematical formulation

# Formulation: General setting<sup>6</sup>

Consider an aggregate of  $N$  pigments interacting with its surrounding proteins. Assume that

- The analysis of the electronic configuration is reduced to the valence electrons
- There are only two states, excited and ground, and the EET follows the Donor–Acceptor scheme



- Scale of the problem  $\Rightarrow$  quantum approach.

<sup>6</sup> V. May, O. Kühn: CHARGE AND ENERGY TRANSFER DYNAMICS IN MOLECULAR SYSTEMS, VILEY-VCH, 2011

# Evolution of the full system

The aggregate+proteins system evolves according to

$$i \hbar \partial_t |\Psi\rangle = \mathcal{H} |\Psi\rangle, \quad \text{where} \quad |\Psi\rangle = |\Psi\rangle(t; r; R; Z)$$

is the wavefunction of the system,  $t > 0$  is the time,

- $r = (r_1, \dots, r_N)$  are the electronic coordinates,
- $R = (R_1, \dots, R_N)$  are the nuclear coordinates,
- $Z = \{Z_k\}_{k \in K}$  are the reservoir coordinates, and

$$\mathcal{H} = H_{agg}(r; R) + H_P(Z) + H_{agg-P}(r; R; Z), \quad \text{with}$$

$$H_P = \frac{1}{2} \sum_{k \in K} (T_k + \omega_k^2 m_k Z_k^2), \quad H_{agg-P} = \sum_{k \in K} f_k(R) Z_k$$

being the reservoir and interaction Hamiltonians, resp.

# Formulation: The aggregate Hamiltonian

$$H_{agg} = \sum_{n=1}^N H_n + \frac{1}{2} \sum_{m,n=1}^N V_{nm}, \quad \text{where}$$

- $H_n$ : Intramolecular Hamiltonian of the  $n^{th}$  pigment
- $V_{mn}$ : intermolecular Coulomb interactions

Neglecting the electrostatic coupling among different molecules and setting the ground energy to be 0, we have

$$H_{agg} = H_{agg}^{(1)} + H_{agg}^{(2)} + \dots + H_{agg}^{(N)}, \quad (1)$$

$$H_{agg}^{(1)} = \sum_{n=1}^N E_n |n\rangle \langle n| + \frac{1}{2} \sum_{m \neq n=1}^N J_{nm} |m\rangle \langle n|, \quad (2)$$

$E_n$  = site energies,  $J_{nm}$  = Coulombian interaction.



# Relevant models of EET<sup>7</sup>

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<sup>7</sup>T. Renger, *Photosynth. Res.* 102:471-485, 2009

# Förster theory: Assumptions

- T. Förster<sup>8</sup> proposed that EET is transferred by Coulombian interaction
- If the extension of the molecular wavefunction is smaller than the intermolecular distance  $|X_{nm}|$ , then

$$J_{nm} = \kappa_{nm} \frac{|d_n||d_m|}{|X_{nm}|} \text{ (dipole-dipole approximation),}$$

where  $\kappa_{nm}$  is an orientation factor depending on the dipole moments  $d_j$

- **If the exciton-vibrational coupling is much larger than the Coulombian one, then the excited states are localized and incoherent (hopping) transfer happens.**

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<sup>8</sup> *Ann. Phys. Leipzig*, 2:55-75, 1948

# Förster theory: Rate constants

For  $P_n(t)$  = Probability of system to be in the state  $|n\rangle$ ,

## Förster formulae for the EET

$$P'_n(t) = \sum_{m=1}^N k_{m \rightarrow n} P_m(t) - \sum_{m=1}^N k_{n \rightarrow m} P_n(t),$$

$$k_{n \rightarrow m} = \frac{2\pi}{\hbar^2} |J_{nm}|^2 \int_{\mathbb{R}} D_{\alpha}^{(m)}(\omega) D_I^{(n)}(\omega) d\omega,$$

$D_{\alpha}^{(m)}$  = absorbance lineshape function of the acceptor

$D_I^{(n)}$  = emission lineshape function of the donor.

EET governed by these rules is also known as Förster Resonance Energy Transfer (FRET).

# Quantum coherence defeats Förster theory

- Förster theory is **applicable only for few photosynthetic systems**. The EET in peridinin-Chla complex of dinoflagellates<sup>9</sup> is an example of successful application.
- It is observed long-lasting coherence  $\Rightarrow$  **The assumption of localized excited states is, in general, not suitable**

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<sup>9</sup>Kleima et al., *Biophysics J.*, 78:344-353, 2000



# Weak coupling: Frenkel excitons

If the exciton-vibrational coupling is much weaker than the Coulombian interaction, then

- $\mathcal{H} \approx H_{agg}$
- $J_{nm}$  couplings become relevant and the localized excited states  $|n\rangle$  do not diagonalize  $H_{agg}$  anymore

We consider the eigenstates  $|\alpha\rangle$  of  $H_{agg}$ . Since

$$|\alpha\rangle = \sum_{n=1}^N c_n^\alpha |n\rangle,$$

which is a coherent superposition of the localized excited states, we conclude that **weak coupling induces delocalized excited states**, known as **Frenkel excitons**, associated with the **exciton energies**  $\varepsilon_\alpha$

# Redfield theory: Rate constants

Multilevel Redfield theory<sup>10</sup> can be applied:

Redfield rates (Renger et al, *Phys.Rep.* 343:138-254, 2001)

$$P'_\alpha(t) = \sum_\beta k_{\beta \rightarrow \alpha} P_\beta(t) - \sum_\beta k_{\alpha \rightarrow \beta} P_\alpha(t),$$

$$k_{\alpha \rightarrow \beta} = 2\gamma_{\alpha\beta}\pi^2 \{ [1 + n(\omega_{\alpha\beta})] J(\omega_{\alpha\beta}) + n(-\omega_{\alpha\beta}) J(-\omega_{\alpha\beta}) \}$$

$$\gamma_{\alpha\beta} = \sum_{m,n=1}^N e^{-f(K, |R_n - R_m|)} c_m^{(\alpha)} c_m^{(\beta)} c_n^{(\alpha)} c_n^{(\beta)}, \quad \hbar\omega_{\alpha\beta} = \varepsilon_\alpha - \varepsilon_\beta$$

- $f = f(K, \delta)$  is a  $\delta$ -decreasing function
- $J(\omega)$  is the spectral density (extended by 0 for  $\omega < 0$ )
- $n(\omega)$  is the Bose-Einstein distribution function

<sup>10</sup>IBM J. Res. Dev. 1:19-31, 1957

# Redfield theory: Applications

This model has been successfully applied to model EET:

- In simple dimeric structures by M. Yang, G. Fleming<sup>11</sup> and by P. Kellberg, T. Pullerits<sup>12</sup>
- In bacterias by T. Renger et al. for the WSCP complex<sup>13</sup> and by J. Adolphs et al. for the FMO complex<sup>14</sup>
- In higher plants by O.Kühn et al.<sup>15</sup> and by V. Prokhorenko, A. R. Howard<sup>16</sup>

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<sup>11</sup> *Chem. Phys.* 275: 355-372, 2002

<sup>12</sup> *J. Chem. Phys.*, 124: 1-9, 2006

<sup>13</sup> *J. Phys. Chem. B*, 111(35): 10487-10501, 2007

<sup>14</sup> *Photosynth. Res.* 95: 197-209, 2006

<sup>15</sup> *Chem Phys*, 275:15-30, 2002

<sup>16</sup> *J. Phys. Chem. B*, 104: 11563-11578, 2000



# 'Equilibrate' coupling regime

# Discussion

The type of EET hinges upon two time scales:

Intramolecular relaxation time  $\tau_{rel}$  and transfer time  $\tau_{trans}$ .

- If  $\tau_{rel} \ll \tau_{trans}$ , the excitation cannot persist in two different molecules  $\Rightarrow$  *incoherent transfer*, associated with classical probabilities
- If  $\tau_{trans} \ll \tau_{rel}$ , excitation moves around the aggregate  $\Rightarrow$  *coherent transfer*, associated with quantum probabilities
- If  $\tau_{trans} \approx \tau_{rel} \Rightarrow$  *partially coherent transfer* (equilibrate exciton-vibrational coupling).

**How can we model EET in this case?**

# Equilibrate coupling: Modified Redfield theory

## Modified Redfield Theory

- Considers delocalized states (strong excitonic coupling)
- Introduces reorganization effects in the nuclear Hamiltonian, which are caused by interaction with proteins (strong exciton-vibrational coupling).

It has been applied by V. Novoderezhkin et al. for EET

- in the FMO complex<sup>17</sup>
- in PS II of higher plants<sup>18</sup>

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<sup>17</sup> *J Phys Chem B*, 109: 10493-10504, 2005

<sup>18</sup> *Biohys J*, 89: 1464-1481, 2005

# Combined coupling: Generalized Förster rates

There are large complexes where delocalized excited states are formed only in certain domains.

- Within these domains, Redfield theory can be used
- To describe transfer between excitons in different domains, Förster theory is extended

## Generalized Förster rates

*Transfer between  $|\alpha_a\rangle$  and  $|\beta_b\rangle$  in the domains  $a$  and  $b$ :*

$$k_{\alpha_a \rightarrow \beta_b} = 2\pi \frac{|V_{\alpha_a \beta_b}|^2}{\hbar^2} \int_{\mathbb{R}} D_{\alpha_a}(\omega) D_{\beta_b}(\omega) d\omega,$$

$$V_{\alpha_a \beta_b} = \sum c_{m_a}^{\alpha_a} c_{n_b}^{\beta_b} V_{m_a n_b}$$

Applications: Green sulfur bacteria and PS II in plants

# Prospects

In order to provide EET with a rigorous mathematical treatment, we are interested in

- Achieving a suitable functional framework for the wavefunctions and operators involved in such processes
- Finding out an appropriate master equation in the Lindblad form for EET
- Analyzing the meaning of the Wigner transform in this scope, in order to apply the mathematical tools of PDEs to coherent ET theories
- Studying the suitability of a stochastic wavefunction approach to EET<sup>19</sup>

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<sup>19</sup>L. Diosi, W.T. Strunz, *Physics Letters A*, 235:569-573, 1997;





Thank you!!