A microscopic model for resonant energy transfer between molecules

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Photosynthesis

Photosynthesis is an amazingly efficient mechanism for trapping photons, and converting energy into mechanical and chemical form. It works even with low intensity photon sources, e.g. hydrothermal vents at depths of 2.5 km!

Green sulfur bacteria

Specialized components in the cell perform photosynthesis.

Photon capture

Photosynthesis division of labor: photon capture and energy conversion occur in different units. Needs efficient excitation transfer between molecular units in the cell.
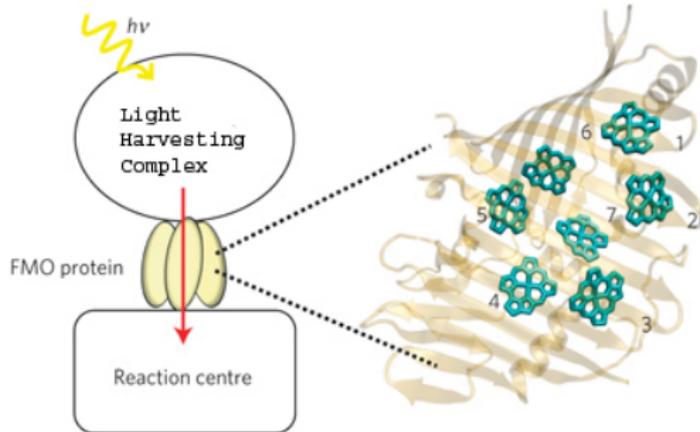
Fenna-Matthews-Olson complex in green sulfur bacteria

Composed of 7 molecular units: excitation migrates from the antennae (units 1,6) to the reaction center (unit 3).
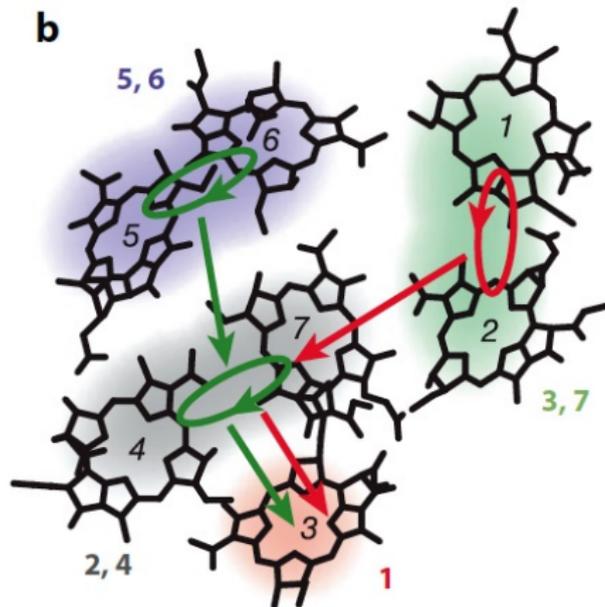
Fenna-Matthews-Olson complex

Modeled as array of 7 coupled 'spins': mini quantum spin system! Highly efficient and robust at room temperature with noisy environment.
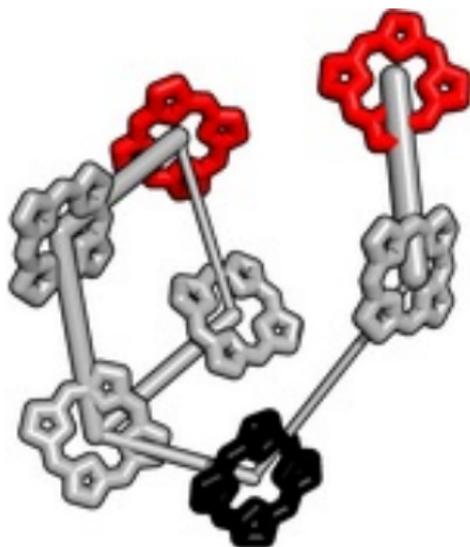
Theory

Goals: develop ab initio model for exciton transport across a system like the FMO complex. Calculate transfer rate and efficiency. Look for evidence of evolutionary selection via optimization strategies.

Evaluate possibility of quantum coherence over timescales of $\sim 100's$ *fs*.

Exciton transport: resonant energy transfer

Photon absorption at the antenna produces a localized exciton. In first approximation, this couples to other units through the dipole-dipole interaction:

$$J_{j,k} = \alpha \, \frac{\left[\mu_j \cdot \mu_k - 3(\mu_j \cdot \hat{\mathbf{R}})(\mu_k \cdot \hat{\mathbf{R}}) \right]}{R^3}$$

μ_j is the electric dipole moment at unit j:

$$\mu_j = e \int \overline{\psi_e}(\mathbf{x}) \, x_j \, \psi_g(\mathbf{x}) \, d\,\mathbf{x}$$

Exciton transport: resonant energy transfer

The interaction occurs in the near-field region, and can be described as exchange of a virtual photon:
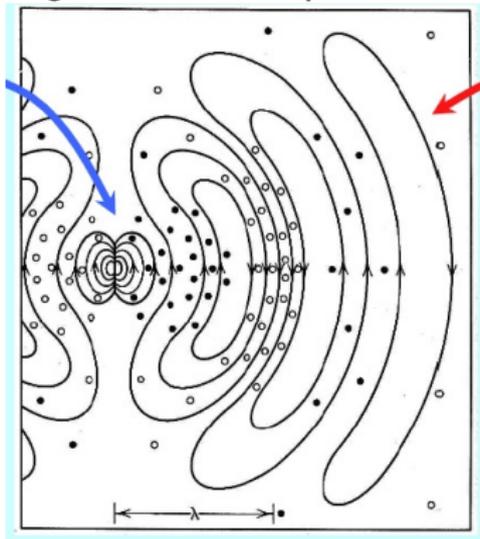
Basic 2-state model

Each dipole is modeled as a qubit, where the two states represent the ground and excited states of the unit. The full state space is

$$\mathcal{H} = \left(\mathbb{C}^2\right)^{\otimes N}$$

The one-exciton subspace $\mathbb{C}^N$ is invariant under the dynamics, and the restricted Hamiltonian is $H = (H_{j,k})$ with

$$H_{j,k} = E_j\,\delta_{j,k} + J_{j,k}$$

The dynamics in this subspace is calculated using a master equation:

$$\frac{d\rho}{dt} = -i[H, \rho] + \sum_j \mathcal{L}_j(\rho) \tag{1}$$

where $\mathcal{L}_j$ are Lindblad operators representing fluorescent decay for each system.

Basic 2-state model

Conclusion: on-resonance transfer occurs with inverse timescale proportional to coupling strength $J_{j,k}$.

The 2-state model predicts that coherent transfer occurs at a rate proportional to the coupling J, and hence

$$\kappa_{RET} \sim R^{-3}$$

This transfer occurs in competition with the fluorescent decay. Comparing these rates leads to a distance scale for energy transport, namely

$$D_{RET} \sim \lambda$$

where λ is the wavelength of the fluorescent photon.

This predicts a length scale of hundreds of *nm*, which is too large by several orders of magnitude (compared to experimental results).

Förster's theory

By considering an ensemble of donor and acceptor molecules and using statistical methods, Förster derived the following rate formula with the inverse sixth power of separation:

$$\kappa_{FRET} = \frac{1}{\tau_D} \left(\frac{R_0}{R} \right)^6$$

Here τ_D is the fluorescent lifetime of the donor molecule, and R_0 is the FRET distance (for which Förster provided an explicit formula).

This formula predicts a length scale of approximately $5 \sim 10$ *nm*, with a sharp falloff due to the inverse sixth power. The numerical factors are very accurate, and there is excellent agreement with experiment.

FRET as molecular ruler

FRET is an important tool in protein analysis, where it provides an accurate way to measure distance: the inverse sixth power makes it highly sensitive to separation.
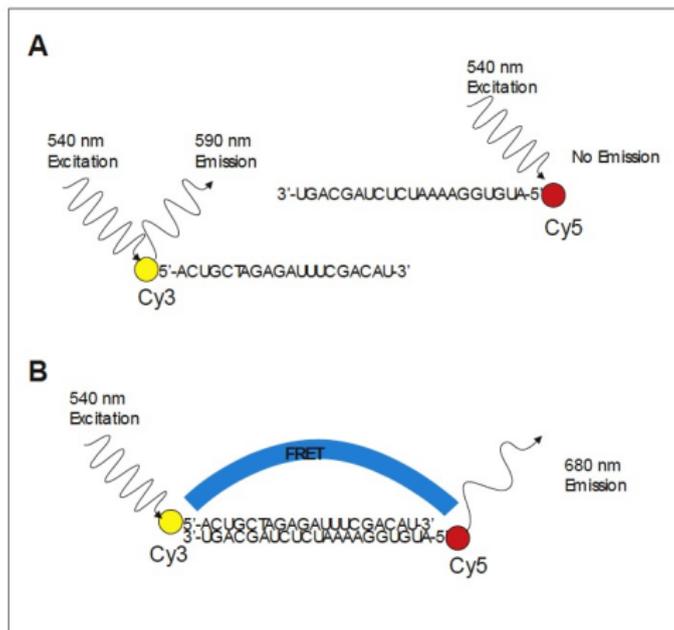
Microscopic model for FRET

Excited state sits in a band of closely spaced vibrational and rotational energy levels. Simplest model: donor exciton couples to *continuous* band in the acceptor. The one-exciton subspace is

$$\mathcal{H} = \mathbb{C} \oplus L^2(\mathbb{R})$$

The Hamiltonian is

$$H = \begin{pmatrix} E_D & V_F \langle f | \\ V_F | f \rangle & h \end{pmatrix} \tag{2}$$

where E_D is the energy of the donor excited state, $f \in L^2(\mathbb{R})$ is the wave packet in the excited band of the acceptor induced by the dipole-dipole interaction term, V_F is the coupling strength, and h is the one-particle Hamiltonian in the excited band.

Model for FRET
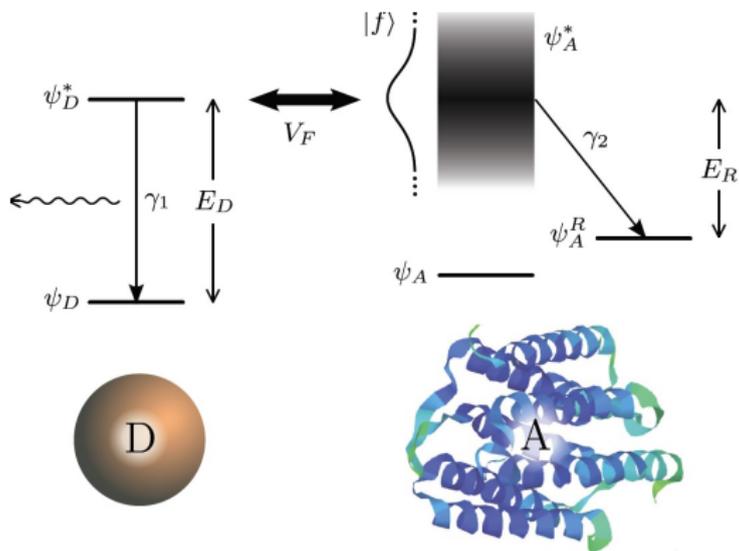
Model for FRET

This is similar to a resonance model, namely a perturbation of an eigenvalue embedded in continuous spectrum. The eigenvalue 'dissolves' in the continuous spectrum, and for weak coupling its decay rate is given by Fermi's Golden Rule. Let $|\psi_0\rangle$ be the initial excited state, then

$$\langle\psi_0|e^{-itH}|\psi_0\rangle \to 0 \tag{3}$$

with approximate exponential decay over an intermediate time scale.

In leading order the rate of decay is $2\pi|f(E_D)|^2\,\sigma(E_D)$, where $\sigma(E)$ is the density of states at energy E.

Full model

The acceptor: discrete ground state ψ_A, a band of closely spaced excited states labelled $\psi_A^*(\varepsilon)$, and a second discrete state ψ_A^R for the acceptor's state after relaxation.

The donor: initialized in a metastable state ψ_D^*, decays to its ground state ψ_D, losing energy either through FRET to the acceptor, or by natural fluorescence via an emitted photon.
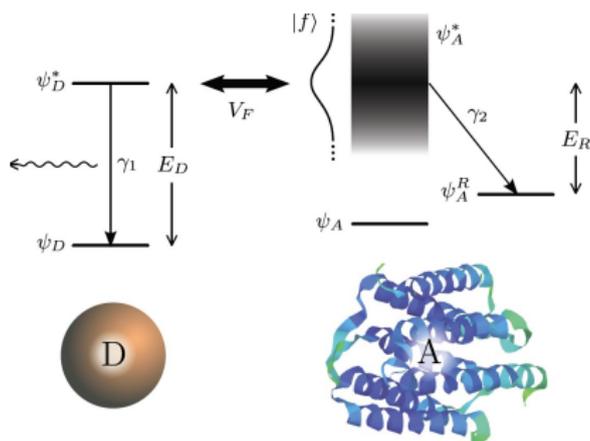
The interaction: transition amplitude for FRET between states ψ_D^*, ψ_A and $\psi_D, \psi_A^*(\varepsilon)$ is

$$F(\varepsilon) = \langle \psi_D^* \psi_A | V_C | \psi_D \psi_A^*(\varepsilon) \rangle \propto R^{-3} \tag{4}$$

Normalized wave packet in excited band:

$$|f\rangle = V_F^{-1} \sum_\varepsilon F(\varepsilon) |\psi_A^*(\varepsilon)\rangle$$

where V_F is a normalization factor which indicates the overall strength of the interaction.

The master equation

$$\frac{d\rho}{dt} = -i[H_D + H_A + H_F, \rho] + \mathcal{L}_D(\rho) + \mathcal{L}_A(\rho) \tag{5}$$

where H_D, H_A are the Hamiltonians of the donor and acceptor, H_F is the FRET coupling defined in (4)

$$H_F = V_F \left(|\psi_D\rangle\langle\psi_D^*| \otimes |f\rangle\langle\psi_A| + |\psi_D^*\rangle\langle\psi_D| \otimes |\psi_A\rangle\langle f| \right)$$

and $\mathcal{L}_D$, $\mathcal{L}_A$ are Lindblad operators representing the fluorescence of the donor and relaxation of the acceptor respectively:

$$\mathcal{L}_D(\rho) = \frac{\gamma_D}{2} \left(2J_D\rho J_D^\dagger - \left\{\rho, J_D^\dagger J_D\right\} \right) \tag{6}$$

$$\mathcal{L}_A(\rho) = \sum_\varepsilon \frac{\gamma_A(\varepsilon)}{2} \left(2J_A(\varepsilon)\rho J_A(\varepsilon)^\dagger - \left\{\rho, J_A(\varepsilon)^\dagger J_A(\varepsilon)\right\} \right)$$

γ_D = rate of donor fluorescence
$J_D = |\psi_D\rangle\langle\psi_D^*| \otimes I_A$ = jump operator for the donor's fluorescence from $|\psi_D^*\rangle$ to $|\psi_D\rangle$

$\gamma_A(\varepsilon)$ = rate of acceptor's relaxation
$J_A(\varepsilon) = I_D \otimes |\psi_A^R\rangle\langle\psi_A^*(\varepsilon)|$ = jump operator for acceptor's relaxation from $|\psi_A^*(\varepsilon)\rangle$ to $|\psi_A^R\rangle$

It is assumed here that each energy level $|\psi_A^*(\varepsilon)\rangle$ separately and incoherently relaxes to $|\psi_A^R\rangle$, at its own rate $\gamma_A(\varepsilon)$. The master equation (5) is a higher-dimensional version of the well-known amplitude-damping channel which describes spontaneous photon emission from a 2-state atom.

Efficiency

The FRET efficiency E is defined as the amount of quenching of the donor's fluorescence which is produced by the FRET coupling when the system starts in the initial state $|\psi_D^* \psi_A\rangle$: $\rho(0) = |\psi_D^* \psi_A\rangle\langle\psi_D^* \psi_A|$ and

$$E = 1 - \lim_{t\to\infty} \langle\psi_D \psi_A|\rho(t)|\psi_D \psi_A\rangle \qquad (7)$$

The FRET distance scale R_0 is defined as the largest separation R for which E is at least 0.5, that is

$$R_0 = \sup\{R : E \geq 0.5\} \qquad (8)$$

Solution of the master equation

First consider the master equation (5) without the Lindblad operators. Starting from the initial state $|\psi_D^* \psi_A\rangle$, the solution $\rho(t)$ evolves unitarily in the subspace spanned by the states $|\psi_D^* \psi_A\rangle$, $|\psi_D \psi_A^*(\varepsilon)\rangle$. The solution in this subspace can be written $\rho(t) = \psi(t)\psi(t)^\dagger$ with

$$\psi(t) = \begin{pmatrix} a(t) \\ \phi(t) \end{pmatrix} = e^{-iB_0 t} \begin{pmatrix} a(0) \\ \phi(0) \end{pmatrix} = e^{-iB_0 t} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad (9)$$

where $a(t)$ is the component in the state $|\psi_D^* \psi_A\rangle$, $\phi(t)$ is the component in the subspace spanned by the states $|\psi_D \psi_A^*(\varepsilon)\rangle$, and

$$B_0 = \begin{pmatrix} E_D & V_F\langle f| \\ V_F|f\rangle & h \end{pmatrix} \qquad (10)$$

Here E_D is the donor's excited state energy, and h is the diagonal energy operator acting in the acceptor's excited band: $(h\psi_A^*)(\varepsilon) = \varepsilon\psi_A^*(\varepsilon)$.

Including the Lindblad operators in (5) modifies the operator B_0 by the inclusion of non-hermitian diagonal terms, representing leakage of probability into the states $|\psi_D \psi_A^R\rangle$ and $|\psi_D \psi_A\rangle$. The solution becomes

$$\begin{pmatrix} a(t) \\ \phi(t) \end{pmatrix} = e^{-iBt} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \; B = \begin{pmatrix} E_D - \frac{i}{2}\gamma_D & V_F\langle f| \\ V_F|f\rangle & h - \frac{i}{2}\Pi_A \end{pmatrix} \quad (11)$$

where $\Pi_A = \sum_\varepsilon \gamma_A(\varepsilon) \, |\psi_A^*(\varepsilon)\rangle\langle\psi_A^*(\varepsilon)|$.

This is the solution in the subspace spanned by the excited states $|\psi_D^* \psi_A\rangle$, $|\psi_D \psi_A^*(\varepsilon)\rangle$.

The efficiency is

$$E = 1 - \gamma_D \int_0^\infty |a(s)|^2 \, ds \quad (12)$$

Exact solutions

With some additional assumptions, the solution can be computed using resolvent techniques and analytic continuation:

(i) the excited band is continuous, with spectrum extending from $-\infty$ to $+\infty$ and with constant density of states,
(ii) $\gamma_A(\varepsilon) = \gamma_A$ is constant (decay rate of acceptor into its relaxed state),
(iii) the normalized FRET wavefunction f is the square root of a Lorentzian:

$$f(\varepsilon) = \sqrt{\frac{\gamma}{\pi}} \frac{1}{\varepsilon - E_0 - i\gamma} \tag{13}$$

where E_0 is the center and $\gamma > 0$ is the width of the wavepacket. [valid for a resonance in weak coupling limit]

Exact solutions

This leads to an exact solution for

$$\begin{pmatrix} a(t) \\ \phi(t) \end{pmatrix} = e^{-iBt} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

namely

$$a(t) = \sum_{j=1}^{2} e^{-ip_j t} C_j \tag{14}$$

where p_1, p_2 are resonances (poles of $(z - B)_{11}^{-1}$) below the real axis, and C_1, C_2 are the residues of these poles. The efficiency is

$$E = 1 - \gamma_D \sum_{j,k=1}^{2} \overline{C_j} \, C_k \, \frac{1}{i(\overline{p_j} - p_k)} \tag{15}$$

Application: quantum dot and bacteriorhodopsin

Recent proposal for improved dye-sensitized solar cells: a
mixture of Quantum Dots (QD) and the protein
bacteriorhodopsin (bR).
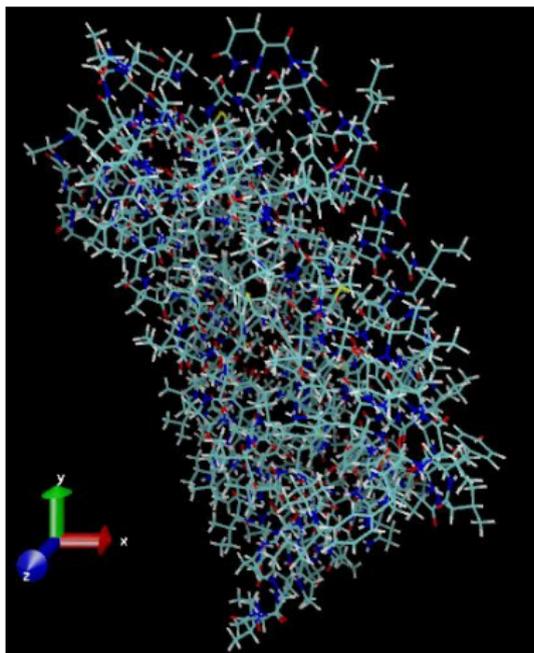
QD and bR

The QD would act as an antenna for photon absorption, with subsequent transfer to the retinal complex in bR. The retinal complex in bR is known to be an efficient absorber of photons through direct capture, and this same efficiency is expected for non-radiative transfer of excitons from QD to bR via the FRET mechanism.

Bacteriorhodopsin (Halobacterium Halobium)

Lys 216   Retinal

Diphosphatidylglycerophosphate lipid
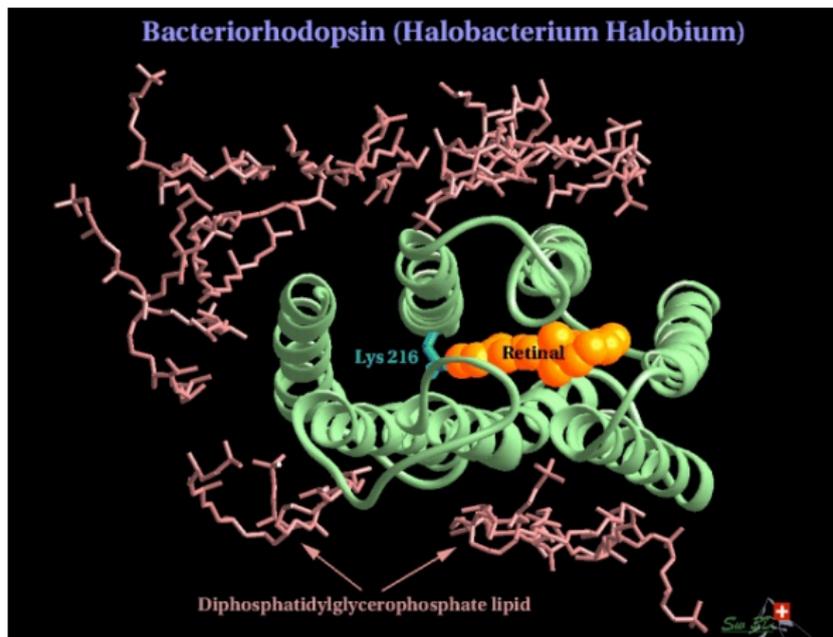
QD and bR

The quantum dot has a band gap of approximately 2 eV. The FRET coupling strength V_F is determined by the formula

$$V_F = \frac{d_{QD}\, d_{bR}}{4\pi\, \epsilon_0\, \epsilon_r\, R^3}\, \alpha \tag{16}$$

where ϵ_r is the permittivity of the medium, R is the separation between the molecules, d_{QD}, d_{bR} are the dipole moments of the QD and bR respectively, and the numerical factor α depends on orientations of dipoles relative to the separation between molecules. In atomic units this gives

$$V_F = \frac{15.479}{R^3} \tag{17}$$

QD and bR

Figure 2 (a) shows the efficiency as a function of R for these values, with varying widths for the Lorentzian wave function.
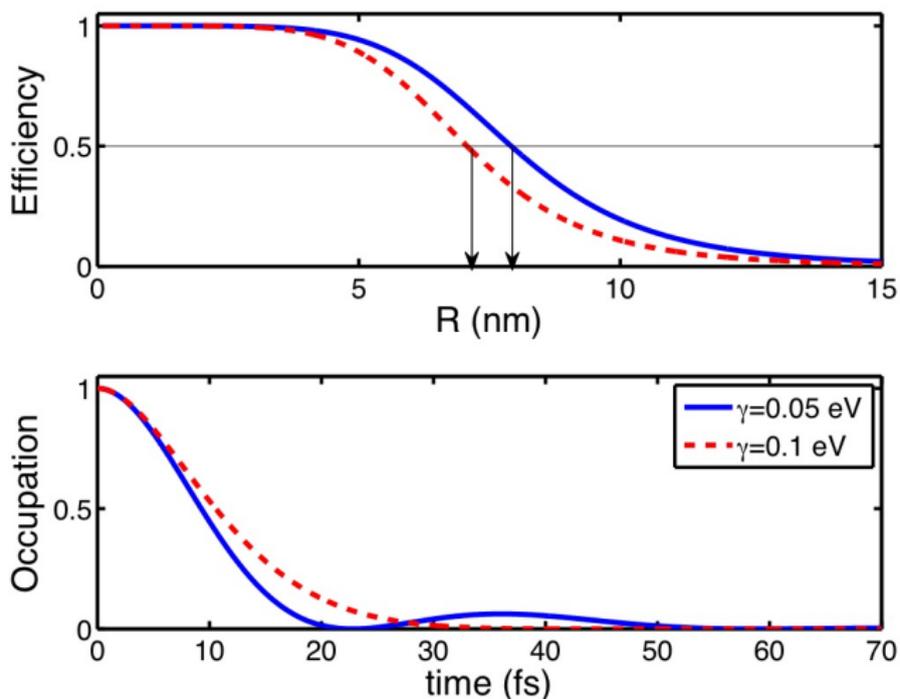
QD-bR

The FRET distance R_0 is estimated to be about $7 - 8$ nm. The curve almost exactly matches the phenomenological formula for efficiency

$$E = \frac{R_0^6}{R_0^6 + R^6}$$

Fermi's Golden Rule predicts a FRET rate $2\pi V_F^2 |f(E_D)|^2$, and this agrees to within 0.5% with Förster's formula $\gamma_D (R_0/R)^6$. These results are robust against changes in γ (width of the Lorentzian)

Figure 2 (b) shows the occupation probability of the initial donor excited state as a function of time, for the same parameter values and with a separation $R = 2$ nm. Coherent oscillations are apparent when $\gamma = 0.05$ eV.

Conclusions and directions

Robust microscopic model for FRET between pairs of molecules.

Extend to a network with multi-hops, and include effects of the environment.

Develop model for FRET from molecule to metallic substrate: important for application to solar cell.

Is efficiency of photosynthesis solely due to exquisitely fine tuning? or is something else going on, for example does quantum coherence play a role??