Making Resonance Energy Transfer Theory more "Coherent"

Seogjoo (Suggy) Jang

Department of Chemistry and Biochemistry

City University of New York,

Queens College and Graduate Center

Queens College

A senior college in the City University of New York (CUNY) system

One of the 25 hottest universities in the US

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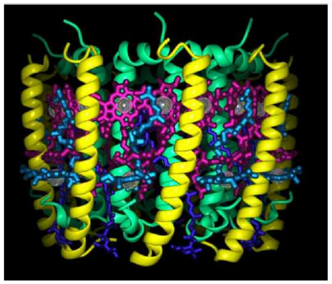
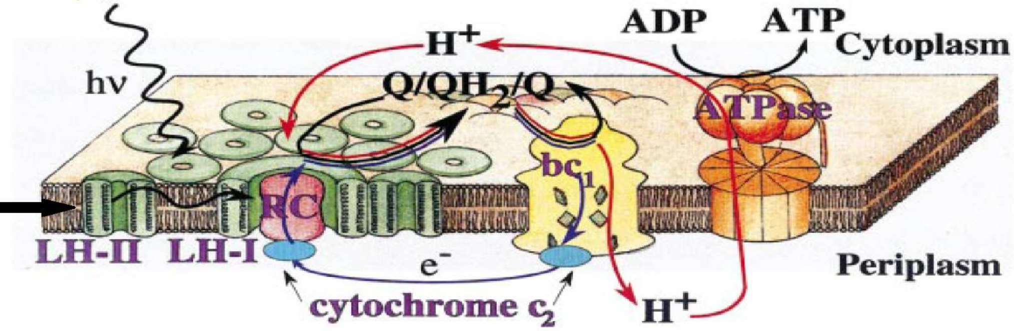
Energy flow in soft optoelectronic systems

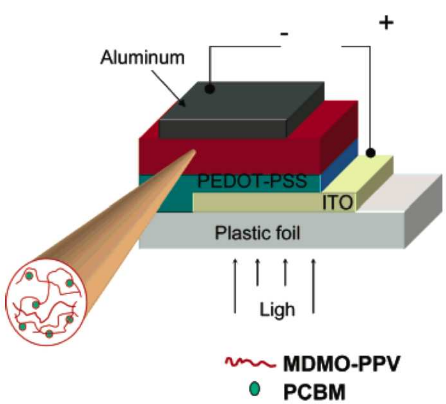
Bacterial photosynthesis

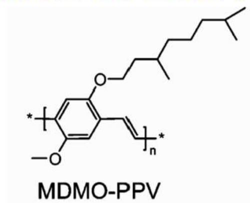


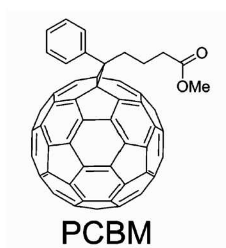


Hu *et al.*, Quart. Rev. Biophys. **35**, 1 (2002)

Plastic solar energy conversion

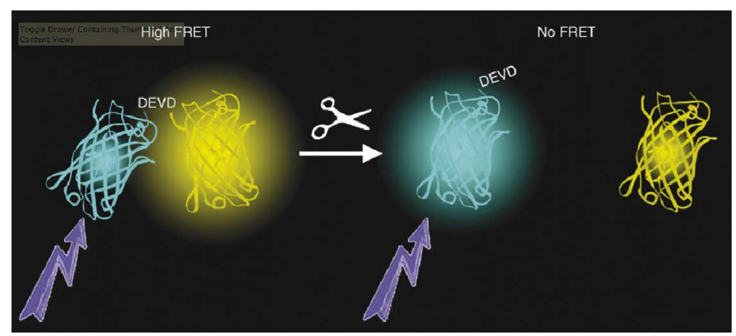






Gunes *et al.*, Chem. Rev. **107**, 1324 (2007)

FRET

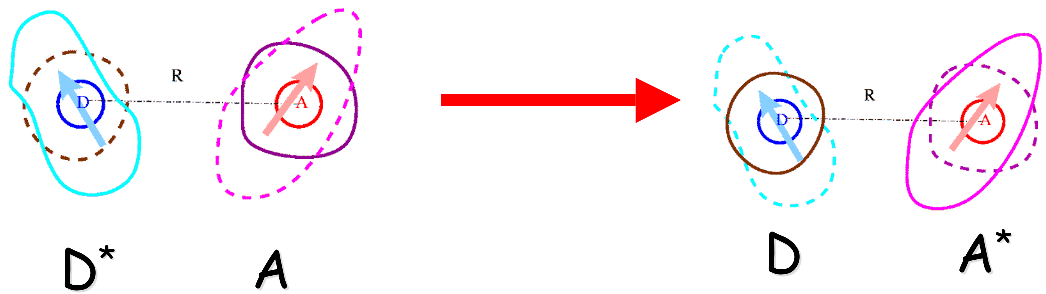


Piston *et al.*, Trends in Biochem. Sci. **32**, 407 (2007)

Förster Theory (FRET)

1910 - 1974

Th. Förster, Ann. Phys. (Leipzig) **6**, 55 (1948)



$$\frac{d[D^*]}{dt} = -\left(\frac{1}{\tau_D} + k_F\right)[D^*]$$

Normalized emission of donor

$$k_F = \frac{9000(\ln 10)\langle\kappa^2\rangle}{128\pi^5 N_A \tau_D n_r^4 R^6}\left(\int d\tilde{\nu}\,\frac{f_D(\tilde{\nu})\epsilon_A(\tilde{\nu})}{\tilde{\nu}^4}\right)$$

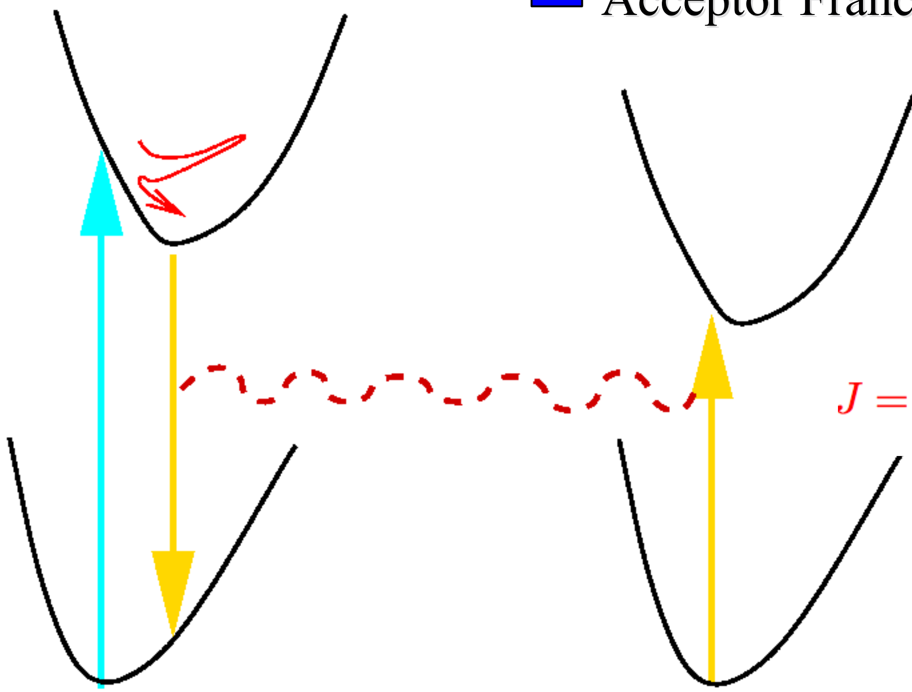
Molar extinction of acceptor

$$\kappa = \hat{\mu}_D \cdot \hat{\mu}_A - 3(\hat{\mu}_D \cdot \hat{\mathbf{R}})(\hat{\mu}_A \cdot \hat{\mathbf{R}})$$

Donor Franck-Condon factor

$$k_F = \frac{\langle J^2 \rangle}{2\pi\hbar^2} \int d\omega L_D(\omega) I_A(\omega)$$

Acceptor Franck-Condon Factor



$$J = \frac{\hat{\mu}_D \cdot \hat{\mu}_A - 3(\hat{\mu}_D \cdot \hat{\mathbf{R}})(\hat{\mu}_A \cdot \hat{\mathbf{R}})}{n_r^2 R^3}$$

$$L_D(\omega) = \frac{3\hbar}{2^5 \pi^3 \tau_D n_r \mu_D^2 c} f_D(\tilde{\nu}) \qquad I_A(\omega) = \frac{3000(\ln 10) n_r \hbar}{(2\pi)^2 N_A \mu_A^2 \tilde{\nu}} \epsilon_A(\tilde{\nu})$$

S. Jang, *J. Chem. Phys.* **127**, 174710 (2007)

When is Förster (or Dexter) Theory Applicable?

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1. Assumption of fully equilibrated excited donor.

2. Donor and acceptor have single electronic centers.

3. No consideration of quantum vibrations of distance or angle.

4. Incoherent quantum kinetics (No coherent return of population).

5. Assumption of macroscopic dieletric response.

Improving Förster (or Dexter) Theory

1. Assumption of fully equilibrated excited donor

   Nonequilibrium extension

2. Donor and acceptor have single electronic centers.

   Multichromophoric extension

3. No consideration of quantum vibration of distance or angle.

   Inelastic extension

4. Incoherent quantum kinetics (No coherent return of population).

   Coherent resonance energy transfer

5. Assumption of macroscopic dieletric response.

   Local field effects

Recent Theoretical Advances

Multichromohporic Effects

H. Sumi, G. Scholes and G. Fleming

Quantum Coherence

R. Silbey, G. Fleming, J. Gilmore and R. H. McKenzie,

S. Mukamel, A. Aspuru-Guzik, G. Scholes

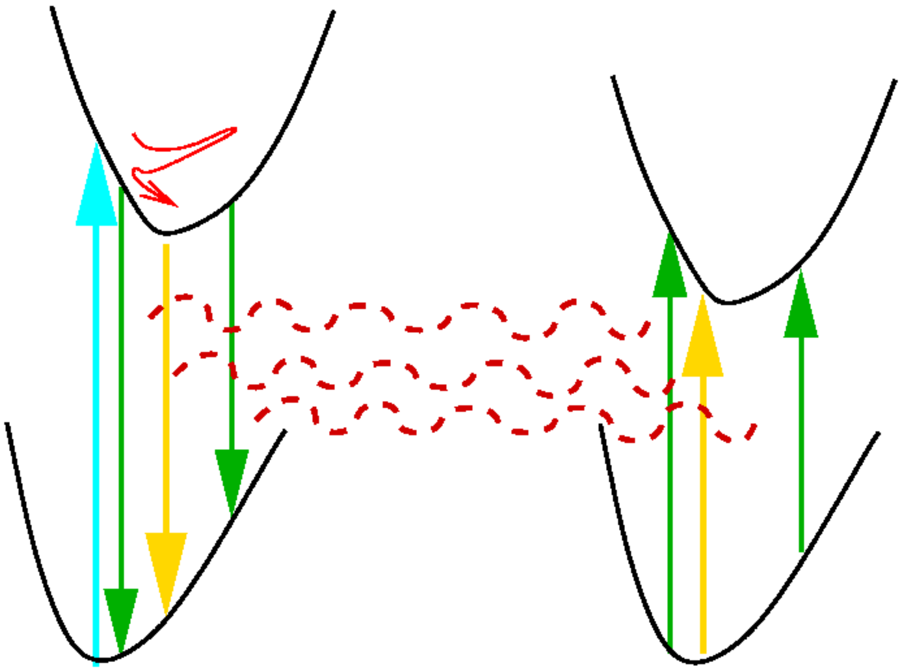
Local Field Effects

R. S. Knox, G. Scholes

Quantum Electrodynamics Formulation

D. L. Andrews

Nonequilibrium FRET

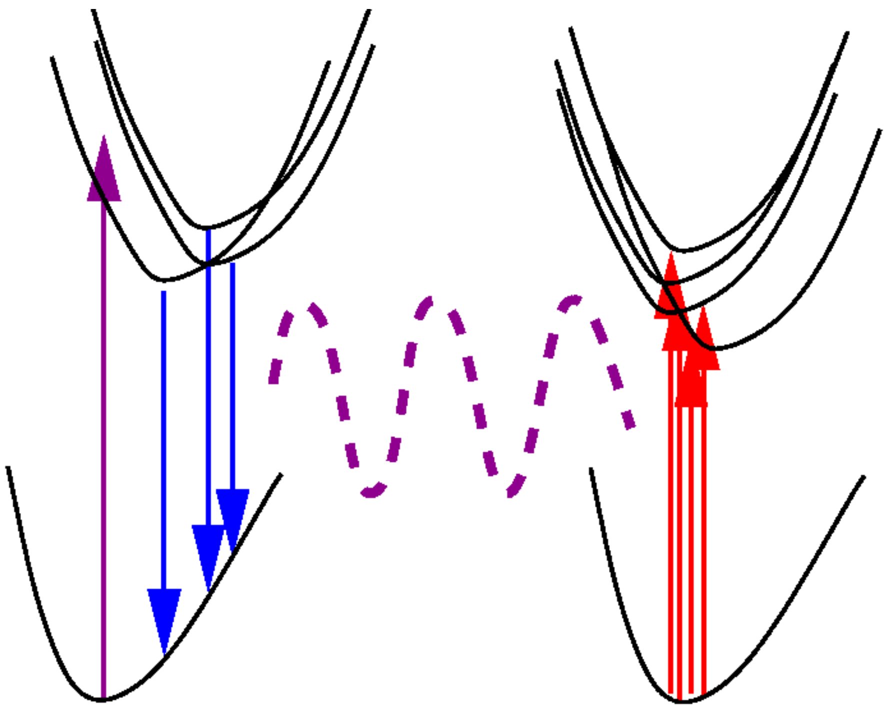


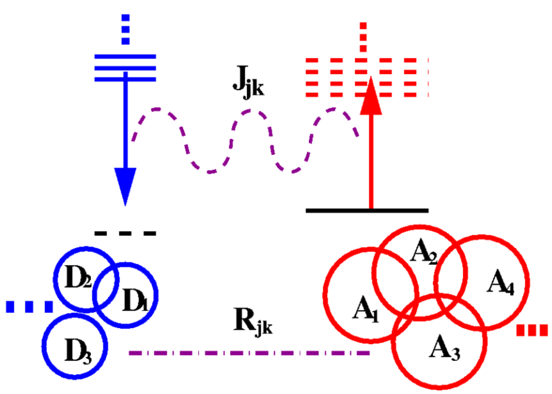
$$k_F(t) = \frac{\langle J^2 \rangle}{2\pi\hbar^2} \int d\omega L_D(t,\omega) I_A(\omega)$$

Jang, Jung, and Silbey, Chem. Phys. **275**, 319 (2002)

Multichromophoric FRET

$$L_D^{j''j'}(\omega) = \int_{-\infty}^{\infty} dt\; e^{-i\omega t} Tr_{_D}\{e^{-iH_D^g t/\hbar}\langle D_{j''}|e^{iH_D^e t/\hbar}\rho_{_D}^e|D_{j'}\rangle\}$$

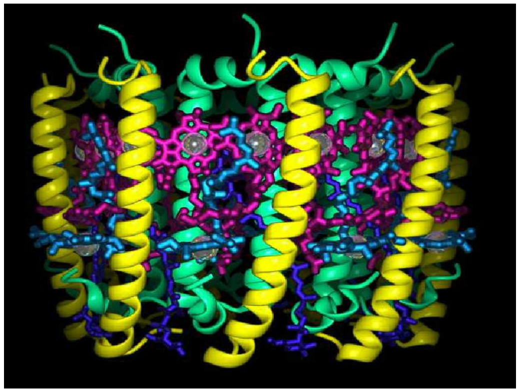


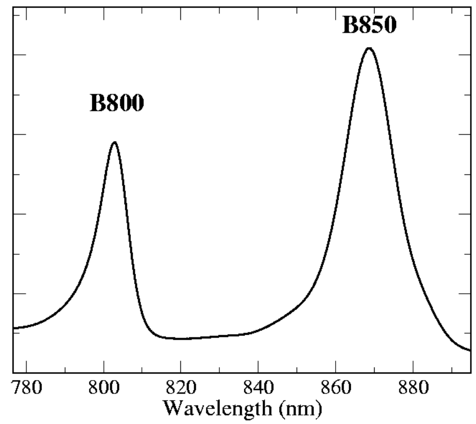


$$I_A^{k'k''}(\omega) = \int_{-\infty}^{\infty} dt\; e^{i\omega t} Tr_{_A}\{e^{iH_A^g t/\hbar}\langle A_{k'}|e^{-iH_A^e t/\hbar}|A_{k''}\rangle\rho_{_A}^g\}$$

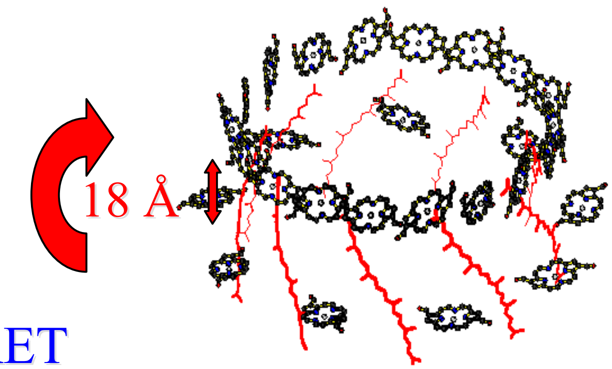
$$k_F^{MC} = \sum_{j'j''}\sum_{k'k''}\frac{J_{j'k'}J_{j''k''}}{2\pi\hbar^2}\int d\omega L_D^{j''j'}(\omega) I_A^{k'k''}(\omega)$$

Jang, Newton, and Silbey, Phys. Rev. Lett. **92**, 218301 (2004)





B800 ➡ B850 Energy Transfer



Theoretical Prediction based on FRET

0.13 ps^{-1} , Fleming et al., *J. Phys. Chem. B* **100**, 6825 (1996)

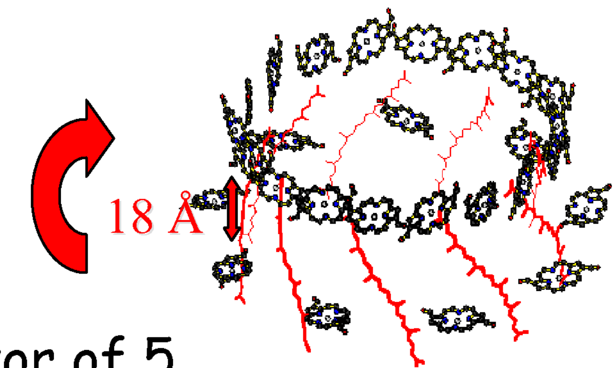
Experimental estimate (Pump-probe spectroscopy)

1.5 ps^{-1} (300 K) - Fleming et al., *J. Phys. Chem. B* **100**, 6825 (1996)

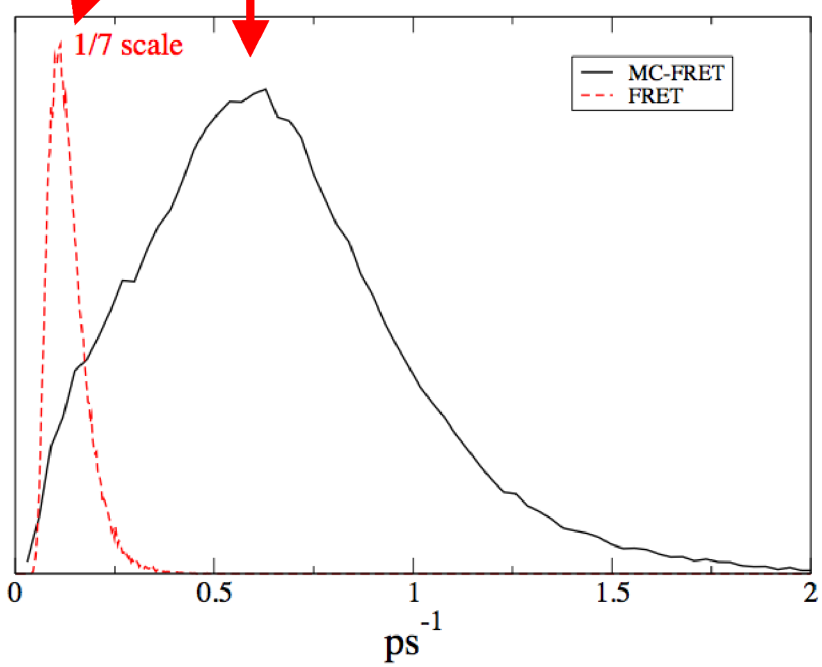
0.7 ps^{-1} (4.2 K) - Sundstrom et al., *J. Phys. Chem. B* **101**, 10560 (1997)

MC-FRET in LH2

B800 ➡ B850 Energy Transfer



Differ by about a factor of 5



Average MC-FRET rate 0.7 ps^{-1} (4.2 K)

$$\mu_{tr} = 6.5 - 7.5 \text{ D for } \epsilon = 1.5 - 2$$

Experiment:

$$\mu_{tr} = 6.4 \text{ D, BChl in acetone}$$

Scherz and Parson, Biochim. Biophys. Acta, **766**, 666 (1984)

Jang, Newton, and Silbey, *J. Phys. Chem. B* **111**, 6807 (2007)

Experimental Evidences for Inelastic Effects and Quantum Coherence

1. Torsional effects and distance modulation

Westenhoff et al., *Phys. Rev. Lett.* **97**, 166804 (2006)

Evidence for torsional relaxation accompanying energy transfer in polythiophene

2. Donor-acceptor quantum coherence

Yamazaki *et al*., *J. Phys. Chem. A*. **106**, 2122 (2002)

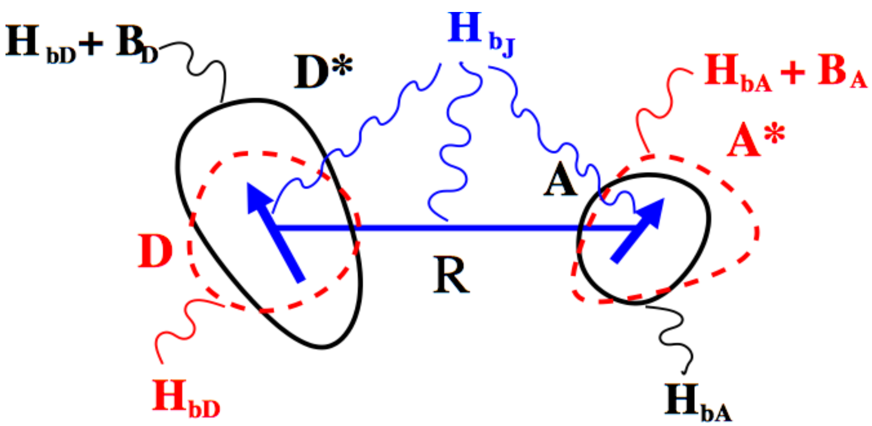
Oscillation in time-resolved anisotropy

Engel *et al*., *Nature* **446**, 782 (2007)

Collini and Scholes, *Science* **323**, 369 (2008)

Evidence of coherence in 2D-electronic spectroscopy

Inelastic FRET - Quantum Mechanical Modulation of Donor and Acceptor Coupling



Inelastic effects can enhance the rate and change the distance dependences.

$$k_s = \frac{9000(ln10)}{128\pi^5 N_A \tau_D \mu_D^2 \mu_A^2} \int d\tilde{\nu} \int d\tilde{\nu}' \frac{f_D(\tilde{\nu})\epsilon(\tilde{\nu}')}{\tilde{\nu}^3\tilde{\nu}'} \tilde{K}_J(\tilde{\nu} - \tilde{\nu}')$$

$$\tilde{K}_J(\tilde{\nu} - \tilde{\nu}') = c \,\mathrm{Re} \int_0^\infty dt\; e^{2\pi i c(\tilde{\nu}-\tilde{\nu}')t} Tr_{b_J} \left\{ e^{iH_{b_J}t/\hbar} J e^{-iH_{b_J}t/\hbar} J \rho_{b_J} \right\}$$

S. Jang, *J. Chem. Phys.* **127**, 174710 (2007)

Coherent resonance energy transfer

$$H = H_s^p + H_s^c + H_{sb} + H_b$$

$$H_s^p = E_D|D\rangle\langle D| + E_A|A\rangle\langle A|$$

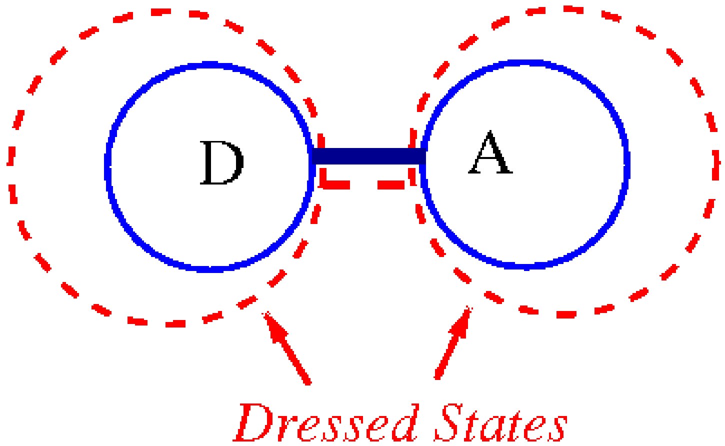
$$H_s^c = J(|D\rangle\langle A| + |A\rangle\langle D|)$$

$$H_{sb} = B_D|D\rangle\langle D| + B_A|A\rangle\langle A|$$

$E_D - E_A, J, B_D,$ and B_A are all comparable.

Fermi's Golden rule or Redfield equation becomes unreliable!

<u>Polaron transformation</u> - renormalizes donor-acceptor coupling



The bath degrees of freedom coupled to donor and acceptor can be included in the newly dressed (cloathed) donor and acceptor states.

The coupling between dressed states can become much weaker.

Holstein, Feynman, Silbey, …

Coherent resonance energy transfer

$$H = H_s^p + H_s^c + H_{sb} + H_b$$

$$H_s^p = E_D|D\rangle\langle D| + E_A|A\rangle\langle A|$$

$$H_s^c = J(|D\rangle\langle A| + |A\rangle\langle D|)$$

$$H_{sb} = B_D|D\rangle\langle D| + B_A|A\rangle\langle A|$$

1. Polaron transformation –> renormalize system-bath coupling
2. Define the fluctuation of renormalized system-bath coupling as a perturbation Hamiltonian
3. 2nd order quantum master equation (QME) with respect to perturbation

Rackovsky and Silbey, *Mol. Phys.* **25**, 61 (1973)

Abram and Silbey, *J. Chem. Phys.* **63**, 2317 (1975)

Coherent resonance energy transfer

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1. Polaron transformation –> renormalize system-bath coupling
2. Define the fluctuation of renormalized system-bath coupling as a perturbation Hamiltonian
3. 2nd order non-Markovian quantum master equation (QME) with respect to perturbation including the effect of nonequilibrium initial condition

Rackovsky and Silbey, *Mol. Phys.* **25**, 61 (1973)

Abram and Silbey, *J. Chem. Phys.* **63**, 2317 (1975)

Quantum Liouville Equation

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}\left[H_s^p + H_s^c + H_{sb} + H_b, \rho(t)\right]$$

$$H_b = \sum_n \hbar\omega_n (b_n^\dagger b_n + \frac{1}{2})$$

$$B_D = \sum_n \hbar\omega_n g_{nD}(b_n + b_n^\dagger)$$

$$B_A = \sum_n \hbar\omega_n g_{nA}(b_n + b_n^\dagger)$$

$$G = \sum_n (b_n^\dagger - b_n)(g_{n_D}|D\rangle\langle D| + g_{n_A}|A\rangle\langle A|)$$ - Generator of polaron transformation

(1) $\tilde{\rho}(t) = e^G \rho(t) e^{-G}$ ← Density operator in the polaronic picture

$$\frac{d\tilde{\rho}(t)}{dt} = -\frac{i}{\hbar}[\tilde{H}_s^p + \tilde{H}_s^c + H_b, \rho(t)]$$

$$\tilde{H}_s^p = \tilde{E}_D|D\rangle\langle D| + \tilde{E}_A|A\rangle\langle A|$$

$$\tilde{H}_s^c = J(\theta_D^\dagger\theta_A|D\rangle\langle A| + \theta_A^\dagger\theta_D|A\rangle\langle D|)$$

$$\tilde{E}_D = E_D - \sum_n g_{nD}^2 \hbar\omega_n$$

$$\tilde{E}_A = E_A - \sum_n g_{nA}^2 \hbar\omega_n$$

$$\theta_D = e^{-\sum_n g_{nD}(b_n^\dagger - b_n)}$$

$$\theta_A = e^{-\sum_n g_{nA}(b_n^\dagger - b_n)}$$

(2) $$\frac{d\tilde{\rho}(t)}{dt} = -\frac{i}{\hbar}[\tilde{H}_0 + \tilde{H}_1, \tilde{\rho}(t)]$$ ← QLE in the polaronic picture

$$\tilde{H}_0 = \tilde{H}_s^p + \langle \tilde{H}_s^c \rangle + H_b = \tilde{H}_{0,s} + H_b$$

$$\tilde{H}_1 = \tilde{H}_s^c - \langle \tilde{H}_s^c \rangle = J(\tilde{B}|D\rangle\langle A| + \tilde{B}^\dagger |A\rangle\langle D|)$$

$$\tilde{B} = \theta_D^\dagger \theta_A - \langle \theta_D^\dagger \theta_A \rangle$$

$$\tilde{\rho}_I(t) = e^{i\tilde{H}_0 t/\hbar} \tilde{\rho}(t) e^{-i\tilde{H}_0 t/\hbar}$$

$$\frac{d\tilde{\rho}_I(t)}{dt} = -\frac{i}{\hbar}[\tilde{H}_{1,I}(t), \tilde{\rho}_I(t)]$$ ← QLE in the interaction and & polaronic picture

$$\tilde{H}_{1,I}(t) = J(\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t))$$

$$\tilde{B}(t) = e^{iH_b t/\hbar} \tilde{B} e^{-iH_b t/\hbar}$$

$$\mathcal{T}(t) = e^{i\tilde{H}_{0,s} t/\hbar} |D\rangle\langle A| e^{-i\tilde{H}_{0,s} t/\hbar}$$

(3) Projection Operator → Quantum Master Equation

S. Jang, J. Cao, and R. J. Silbey, *J. Chem. Phys.* **128**, 114713 (2002)

$$\tilde{\sigma}_I(t) = Tr_b\left\{\tilde{\rho}_I(t)\right\}$$ ← Reduced system density operator

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$ ← Quantum Master Equation

$$\tilde{\sigma}_I(t) = Tr_b\{\tilde{\rho}_I(t)\}$$ ← Reduced system density operator

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$ ← Quantum Master Equation

2nd order approx. $\mathcal{K}(t) = \sum_n \delta g_n^2\{\coth(\frac{\beta\hbar\omega_n}{2})\cos(\omega_n t) - i\sin(\omega_n t)\}, \quad \delta g_n = g_{nD} - g_{nA}$

$$\mathcal{R}(t)\tilde{\sigma}_I(t) = \frac{J^2}{\hbar^2}e^{-\mathcal{K}(0)}\int_0^t d\tau\left\{(e^{-\mathcal{K}(t-\tau)}-1)\left([\mathcal{T}(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)] + [\tilde{\mathcal{T}}^\dagger(t),\tilde{\mathcal{T}}^\dagger(\tau)\sigma_I(t)]\right)\right.$$
$$\left. +(e^{\mathcal{K}(t-\tau)}-1)\left([\mathcal{T}^\dagger(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)] + [\mathcal{T}(t),\mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(t)]\right)\right\} + \text{H. C.}$$

$$\mathcal{T}(t) = e^{i\tilde{H}_{0,s}t/\hbar}|D\rangle\langle A|e^{-i\tilde{H}_{0,s}t/\hbar}$$

S. Jang, Y.-C. Cheng, D. Reichman, and J. D. Eaves, *J. Chem. Phys.*, **129**, 101104 (2008)

$$\tilde{\sigma}_I(t) = Tr_b\{\tilde{\rho}_I(t)\}$$ ← Reduced system density operator

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$ ← Quantum Master Equation

2nd order approx. $\mathcal{K}(t) = \sum_n \delta g_n^2\{\coth(\frac{\beta\hbar\omega_n}{2})\cos(\omega_n t) - i\sin(\omega_n t)\}, \quad \delta g_n = g_{nD} - g_{nA}$

$$\begin{aligned}\mathcal{R}(t)\tilde{\sigma}_I(t) &= \frac{J^2}{\hbar^2}e^{-\mathcal{K}(0)}\int_0^t d\tau\left\{(e^{-\mathcal{K}(t-\tau)}-1)\left([\mathcal{T}(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)] + [\tilde{\mathcal{T}}^\dagger(t),\tilde{\mathcal{T}}^\dagger(\tau)\sigma_I(t)]\right)\right.\\ &\left.+(e^{\mathcal{K}(t-\tau)}-1)\left([\mathcal{T}^\dagger(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)] + [\mathcal{T}(t),\mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(t)]\right)\right\} + \mathrm{H.\,C.}\end{aligned}$$

$$\rho(0) = \sigma(0)e^{-\beta H_b}/Tr\{e^{-\beta H_b}\}, \sigma(0) = |D\rangle\langle D|$$

$$f(t) = e^{2i\sum_n g_{nD}\delta g_n \sin(\omega_n t)}$$

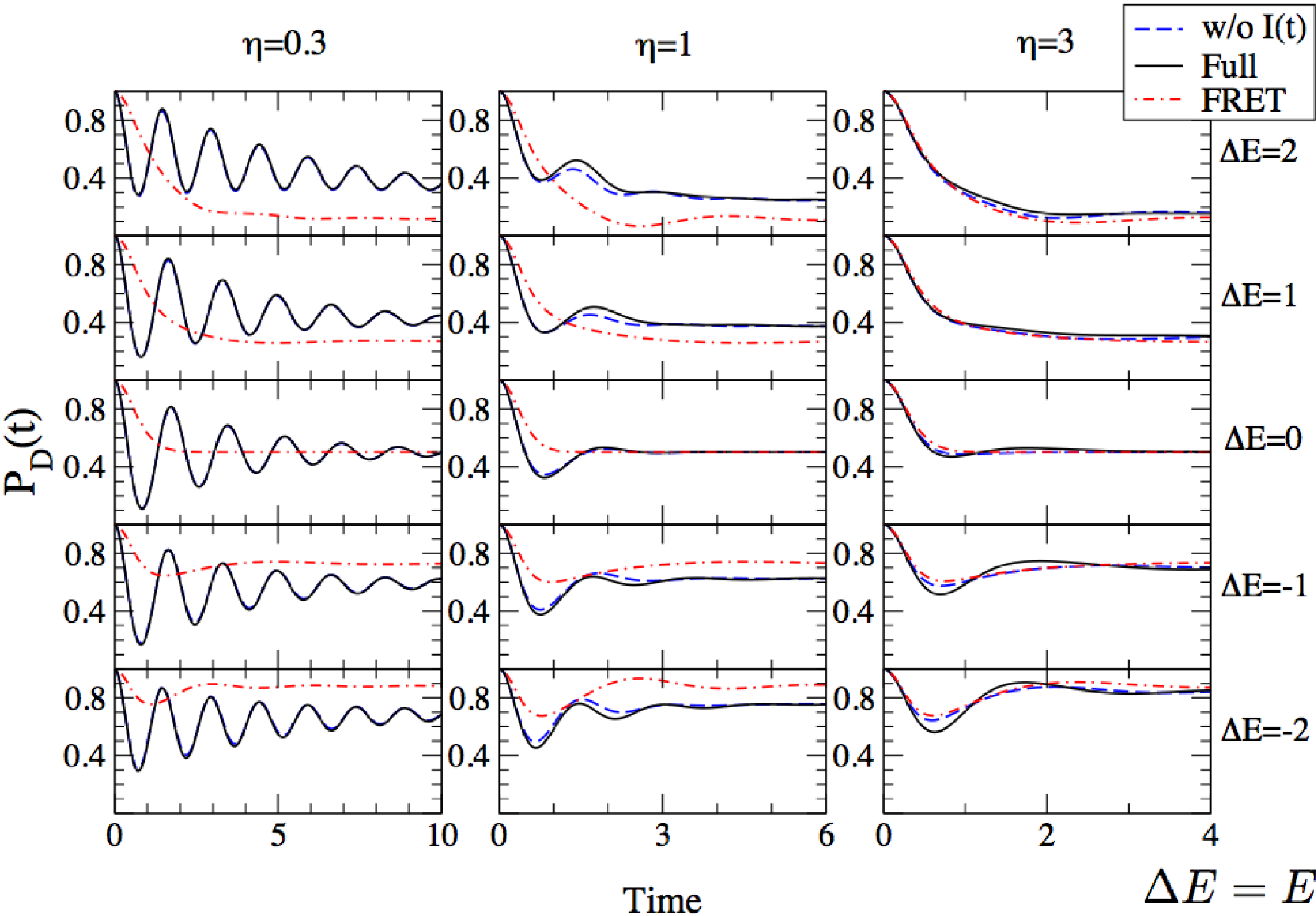
$$\begin{aligned}\mathcal{I}(t) &= -\frac{iJ}{\hbar}e^{-\mathcal{K}(0)/2}(f(t)-1)[\mathcal{T}(t),\sigma(0)]\\ &-\frac{J^2}{\hbar^2}e^{-\mathcal{K}(0)}\int_0^t d\tau\,\{F_{(1)}(t,\tau)[\mathcal{T}(t),\mathcal{T}(\tau)\sigma(0)] + F_{(2)}(t,\tau)[\mathcal{T}^\dagger(t),\mathcal{T}(\tau)\sigma(0)]\\ &+F_{(3)}(t,\tau)[\mathcal{T}(t),\mathcal{T}^\dagger(\tau)\sigma(0)] + F_{(4)}(t,\tau)[\mathcal{T}^\dagger(t),\mathcal{T}^\dagger(\tau)\sigma(0)]\} + \mathrm{H.\,C.}\end{aligned}$$

$$\begin{aligned}F_{(1)}(t,\tau) &= (f(t)f(\tau)-1)e^{-\mathcal{K}(t-\tau)} - f(t) - f(\tau) + 2\\ F_{(2)}(t,\tau) &= (f(-t)f(\tau)-1)e^{\mathcal{K}(t-\tau)} - f(-t) - f(\tau) + 2\\ F_{(3)}(t,\tau) &= (f(t)f(-\tau)-1)e^{\mathcal{K}(t-\tau)} - f(t) - f(-\tau) + 2\\ F_{(4)}(t,\tau) &= (f(-t)f(-\tau)-1)e^{-\mathcal{K}(t-\tau)} - f(-t) - f(-\tau) + 2\end{aligned}$$

S. Jang, Y.-C. Cheng, D. Reichman, and J. D. Eaves, *J. Chem. Phys.*, **129**, 101104 (2008)

$$\hbar = \omega_c = k_B T = 1, J = 2$$

$$\frac{1}{2}\sum_n \delta(\omega - \omega_n)\omega_n^2 \delta g_n^2 = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D} \delta g_n = \frac{\eta}{3!}\frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}$$



$$\Delta E = E_D - E_A$$

FRET: $\frac{d}{dt}P_D^r(t) = -k_{DA}^r(t)P_D^r(t) + k_{AD}^r(t)(1 - P_D^r(t))$

Coherent initial condition

$$\rho(0) = \sigma(0)\rho_b = |I\rangle\langle I|\rho_b$$

$$|I\rangle = I_D|D\rangle + I_A|A\rangle$$

Linear superposition of donor and acceptor excitations

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$

$$\begin{aligned}\mathcal{I}(t) &= -\frac{iJ}{\hbar}\sum_{l=1}^{4}\mathcal{C}_l(t)[\tilde{\mathcal{T}}(t),\tilde{\sigma}_l(0)] \\ &\quad -\frac{J^2}{\hbar^2}\int_0^t d\tau \sum_{l=1}^{4}\Big\{\mathcal{F}_{(1),l}(t,\tau)[\tilde{\mathcal{T}}(t),\tilde{\mathcal{T}}(\tau)]\tilde{\sigma}_l(0) + \mathcal{F}_{(2),l}(t,\tau)[\tilde{\mathcal{T}}^\dagger(t),\tilde{\mathcal{T}}(\tau)]\tilde{\sigma}_l(0) \\ &\quad +\mathcal{F}_{(3),l}(t,\tau)[\tilde{\mathcal{T}}(t),\tilde{\mathcal{T}}^\dagger(\tau)]\tilde{\sigma}_l(0) + \mathcal{F}_{(4),l}(t,\tau)[\tilde{\mathcal{T}}^\dagger(t),\tilde{\mathcal{T}}^\dagger(\tau)]\tilde{\sigma}_l(0)\Big\} + \text{H.C.}\end{aligned}$$

$$\mathcal{C}_1(t) = w(f_D(t) - 1)$$

$$\mathcal{F}_{(1),1}(t,\tau) = w^2\{(f_D(t)f_D(\tau) - 1)e^{-\mathcal{K}(t-\tau)} - f_D(t) - f_D(\tau) + 2\}$$

....

$$f_D(t) = e^{2i\sum_n g_{n_D}\delta g_n \sin(\omega_n t)}$$

$$\mathcal{K}(t) = \sum_n \delta g_n^2\{\coth(\frac{\beta\hbar\omega_n}{2})\cos(\omega_n t) - i\sin(\omega_n t)\}, \quad \delta g_n = g_{nD} - g_{nA}$$

S. Jang, *J. Chem. Phys.* Submitted (2009)

$$\mathcal{J}_D(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_D}{3!}\frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}$$

$$\mathcal{J}_A(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_A}{3!}\frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}$$

$$\mathcal{J}_c(\omega) = -\sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D} g_{n_A} = \frac{\eta_c}{3!}\frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}$$

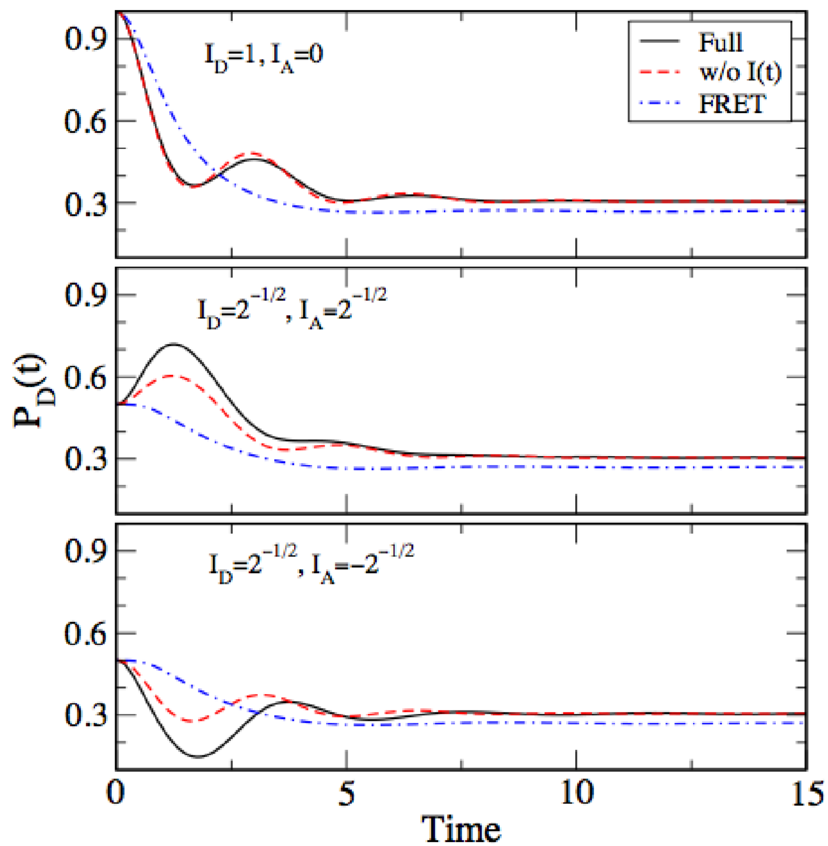
Sensitivity of early nonequilibrium population dynamics on details of initial condition!

$$J = 1$$

$$\eta_D + \eta_c = \eta_A + \eta_c = 1$$

$$E_D - E_A = 1$$

$$|I\rangle = I_D|D\rangle + I_A|A\rangle$$



Units: $\omega_c = \hbar = k_B T = 1$

$$\mathcal{J}_D(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_D}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_A(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_A}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_c(\omega) = -\sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D} g_{n_A} = \frac{\eta_c}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

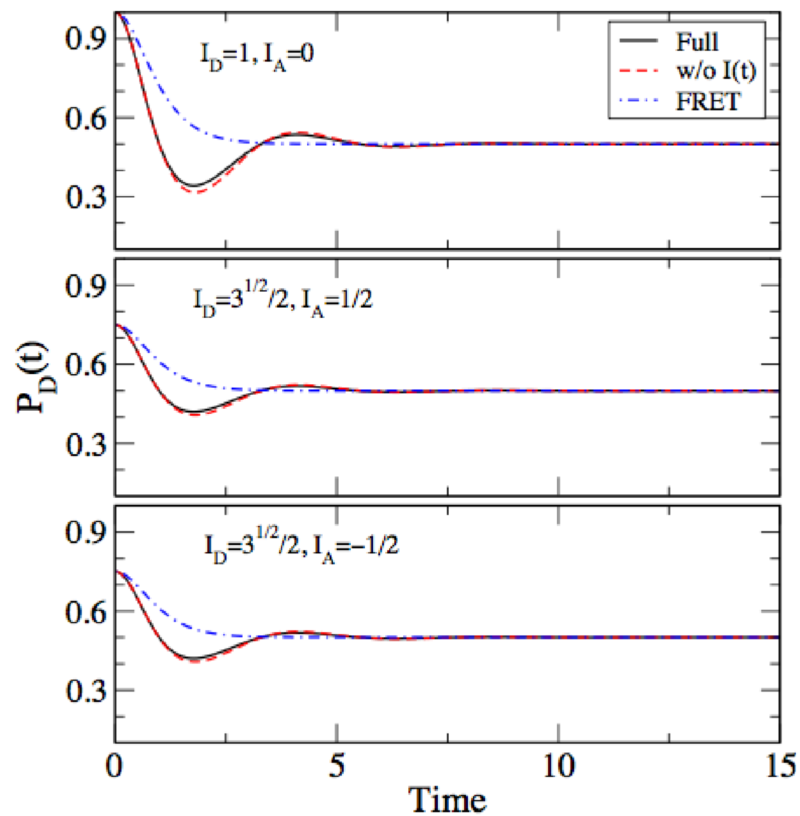
Less sensitive for degenerate donor and acceptor excitation energies

$$J = 1$$

$$\eta_D + \eta_c = \eta_A + \eta_c = 1$$

$$E_D = E_A$$

$$|I\rangle = I_D|D\rangle + I_A|A\rangle$$



Units: $\omega_c = \hbar = k_B T = 1$

$$\mathcal{J}_D(\omega) = \sum_n \delta(\omega-\omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_D}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_A(\omega) = \sum_n \delta(\omega-\omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_A}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_c(\omega) = -\sum_n \delta(\omega-\omega_n)\omega_n^2 g_{n_D} g_{n_A} = \frac{\eta_c}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

Smaller donor-bath coupling results in more population transfer

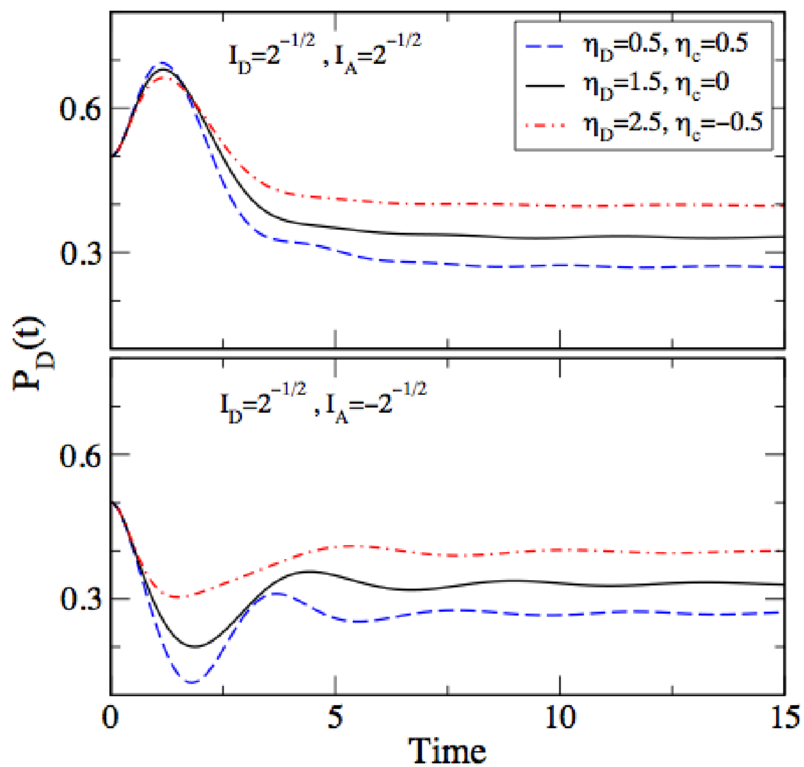
$$J = 1$$

$$\eta_A = 1$$

$$\eta_D + 2\eta_c = 1.5$$

$$E_D - E_A = 1$$

$$|I\rangle = I_D|D\rangle + I_A|A\rangle$$



Units: $\omega_c = \hbar = k_B T = 1$

$$\mathcal{J}_D(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_D}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_A(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D}^2 = \frac{\eta_A}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

$$\mathcal{J}_c(\omega) = -\sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n_D} g_{n_A} = \frac{\eta_c}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$

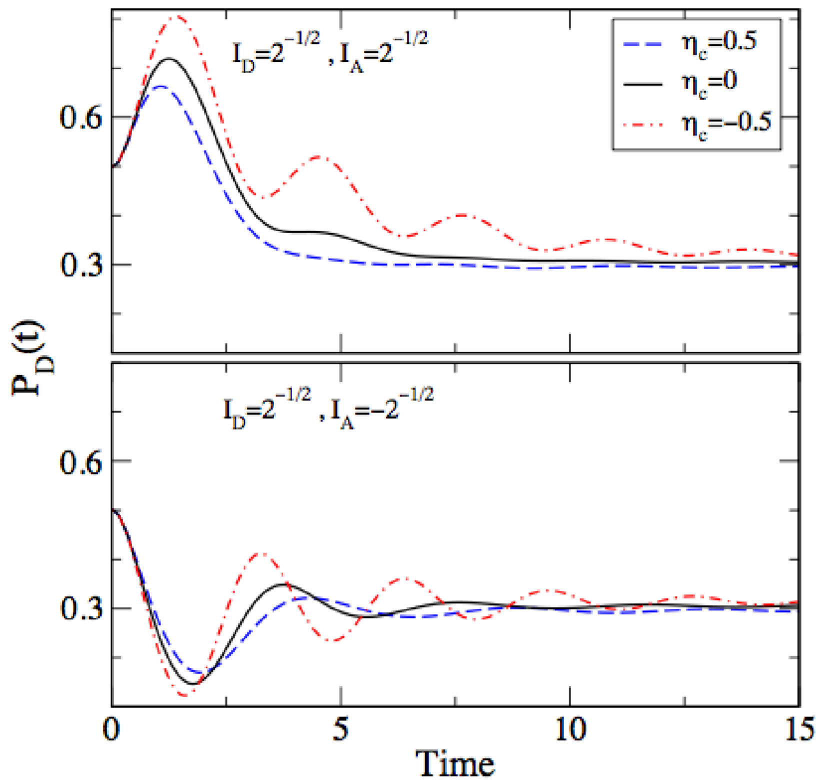
The same sign of common modes results in weak-system bath coupling and protects coherence.

$$J = 1$$

$$\eta_D = \eta_A = 1$$

$$E_D - E_A = 1$$

$$|I\rangle = I_D|D\rangle + I_A|A\rangle$$



Units: $\omega_c = \hbar = k_B T = 1$

Summary

Incoherent Quantum Kinetics

Nonequilibrium,

Multichromophoric, and

Inelastic generalization of FRET

Coherent Resonance Energy Transfer

QME with polaron transformation

- General spectral densities with common modes
- Non-Markovian bath
- Coherent Initial Condition

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