

Dynamics of a Dimer

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Excitation/charge transfer processes

Usually, when a molecule is excited electronically by absorbing a photon, it luminesces by emitting another photon ($\sim 1\text{ns}$).



Fluorescence

However, when another molecule with similar excitation energy is present within tens of nanometers, the excitation can be swapped between the molecules ($\sim 1\text{ps}$).

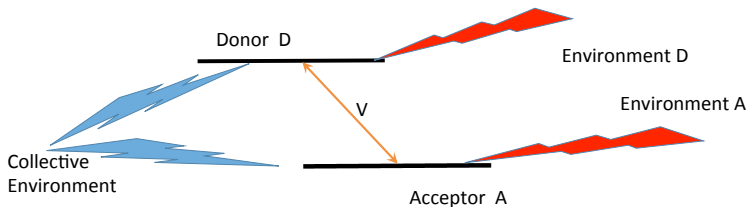


Excitation transfer process: $D^* + A \rightarrow A + D^*$

Excitation transfer happens in **biological systems** (photosynthesis)

Similarly, **charge transport** (electron, proton) happens in chemical redox reactions: $D + A \rightarrow D^- + A^+$ (reactant and product)

Processes take place in noisy environments (molecular vibrations, solvent degrees of freedom)



Local model (red) and collective model (blue)

V : exchange or dipole-dipole interaction

- **Local (uncorrelated) model**: D, A have individual environments
- **Collective (correlated) model**: D, A have common environment

Goal

Derive transfer rate constants in excitation and charge transport processes.

Our main result

We consider a *weakly coupled dimer* (V “small”) and derive the equations of motion of the reduced dimer density matrix (reservoirs traced out), which are:

- valid for all times $0 \leq t \leq \infty$
- valid for all dimer-reservoir coupling strengths
- detailed and explicit, giving relaxation and decoherence rates
- *mathematically rigorous*

Our method

Dynamical Quantum Resonance Theory, in which the reduced dynamics propagator is described by oscillating and decaying directions associated to complex effective energies (=resonances)

Hamiltonian: Collective reservoirs model

Dimer interacts with a single reservoir

$$H_c = \frac{1}{2} \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix} + H_R + \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \otimes \phi(\mathbf{g})$$

$$H_R = \sum_k \omega_k a_k^\dagger a_k, \quad \text{and} \quad \phi(\mathbf{g}) = \frac{1}{\sqrt{2}} \sum_k g_k a_k^\dagger + \text{h.c.}$$

ϵ = D-A energy difference

V = direct matrix element, small: $V \ll \epsilon$

λ_1, λ_2 = dimer-reservoir coupling constants

ω_k = frequency mode k

a_k^\dagger, a_k bosonic creation, annihilation operators

g_k = form factor

Hamiltonian: Local reservoirs model

Donor and acceptor levels interact with individual, independent reservoirs

$$H_I = \frac{1}{2} \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix} + H_{R_1} + H_{R_2} \\ + \lambda_1 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \otimes \phi_1(\mathbf{g}_1) + \lambda_2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \phi_2(\mathbf{g}_2)$$

Initial states, reduced dimer state

Initial states

Taken of the form (collective or local model)

$$\rho_{\text{in}} = \rho_S \otimes \rho_R \quad \text{or} \quad \rho_{\text{in}} = \rho_S \otimes \rho_{R_1} \otimes \rho_{R_2}$$

ρ_S = arbitrary initial density matrix of the dimer

$\rho_R, \rho_{R_1}, \rho_{R_2}$ reservoir equilibrium states at a temperature $T = 1/\beta$

Reduced dimer density matrix

At time t : evolve whole dimer-reservoir density matrix, then trace out the reservoirs:

$$\rho_S(t) = \text{Tr}_{\text{Reservoir}(s)} \left(e^{-itH} \rho_{\text{in}} e^{itH} \right)$$

($H = H_c$ or $H = H_l$, collective or local)

Reservoir spectral function

Effect of single reservoir on dimer encoded in **spectral density**

$$J(\omega) = \sqrt{2\pi} \tanh(\beta\omega/2) \hat{C}(\omega), \quad \omega \geq 0,$$

where

$$\hat{C}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} \mathcal{C}(t) dt$$

is Fourier transform of the symmetrized correlation function

$$\mathcal{C}(t) = \text{Re} \langle e^{itH_R} \phi(\mathbf{g}) e^{-itH_R} \phi(\mathbf{g}) \rangle_{\beta} \quad (\text{thermal average})$$

Our mathematics require **regularity condition** (each reservoir):

$$J(\omega) = \frac{\omega^s}{(1+\omega)^\sigma} \tilde{J}(\omega) \quad \text{with } s \geq 3 \text{ and } \sigma > 3/2$$

$\tilde{J}(\omega)$ = bounded function

(Minimal a priori condition: $s > 1$, super-ohmic; not treatable up to now)

Dimer matrix elements

Dimer site basis for $V = 0$ (or, energy basis)

$$\varphi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \varphi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Population of donor D

$$p(t) = \langle \varphi_1, \rho_S(t) \varphi_1 \rangle = [\rho_S(t)]_{11}, \quad p(0) \in [0, 1]$$

(Population of acceptor = $1 - p(t)$)

Evolution $t \mapsto p(t)$ called **relaxation** while **decoherence** is evolution of off-diagonal element

$$t \mapsto [\rho_S(t)]_{12} = \langle \varphi_1, \rho_S(t) \varphi_2 \rangle$$

Relaxation



Theorem (Population dynamics, relaxation) [M. et al, 2016]

Consider the local/collective reservoirs model. Let λ_1, λ_2 be arbitrary. There is a $V_0 > 0$ s.t. for $0 < |V| < V_0$:

$$p(t) = p_\infty + e^{-\gamma t} (p(0) - p_\infty) + O\left(\frac{t}{1+t}\right),$$

where

$$p_\infty = \frac{1}{1 + e^{-\beta \hat{\epsilon}}} + O(V) \quad \text{with} \quad \hat{\epsilon} = \epsilon - \frac{\alpha_1 - \alpha_2}{2}$$

$\gamma = \text{relaxation rate} \propto V^2$

(different values for local and collective cases)

$\alpha_{1,2} = \text{renormalizations of energies } \pm \epsilon \ (\propto \lambda_{1,2}^2)$

$p_\infty = \text{equil. value w.r.t. renormalized dimer energies}$

Note: Remainder small on time-scale $\gamma t \ll 1$, i.e., $t \ll V^{-2}$

Discussion: **Properties of final donor population p_∞**

$$p_\infty = \frac{1}{1 + e^{-\beta\hat{\epsilon}}} + O(V) \quad \text{with} \quad \hat{\epsilon} = \epsilon - \frac{\alpha_1 - \alpha_2}{2}$$

Increasing acceptor-reservoir coupling increases acceptor population

$$p_\infty \approx \frac{1}{2} - \frac{\hat{\epsilon}}{4T}, \quad \text{for } T \gg |\hat{\epsilon}|.$$

– *Donor strongly coupled:* $\lambda_D^2 \gg \max\{\lambda_A^2, \epsilon\} \Rightarrow \hat{\epsilon} \propto -\lambda_D^2$

Donor pop. p_∞ increases in donor-reservoir coupling λ_D^2

– *Acceptor strongly coupled:* $\lambda_A^2 \gg \max\{\lambda_D^2, \epsilon\} \Rightarrow \hat{\epsilon} \propto \lambda_A^2$

Acceptor pop. $1 - p_\infty$ increases in acceptor-res. coupling λ_A^2

- Effect intensifies at *low temperatures*:

$$p_\infty \approx \begin{cases} 1, & \text{if } \lambda_D^2 \gg \max\{\lambda_A^2, \epsilon\} \\ 0, & \text{if } \lambda_A^2 \gg \lambda_D^2 \end{cases} \quad \text{for } T \ll |\hat{\epsilon}|$$

Acceptor entirely populated if strongly coupled to reservoir at low temp.

Discussion: Relaxation rates

Collective relaxation rate

$$\gamma_c = V^2 \lim_{r \rightarrow 0^+} \int_0^\infty e^{-rt} \cos(\hat{\epsilon}t) \cos \left[\frac{(\lambda_1 - \lambda_2)^2}{\pi} Q_1(t) \right] e^{-\frac{(\lambda_1 - \lambda_2)^2}{\pi} Q_2(t)} dt$$

with

$$Q_1(t) = \int_0^\infty \frac{J(\omega)}{\omega^2} \sin(\omega t) d\omega,$$

$$Q_2(t) = \int_0^\infty \frac{J(\omega)(1 - \cos(\omega t))}{\omega^2} \coth(\beta\omega/2) d\omega$$

Local relaxation rate

$$\begin{aligned} \gamma_l = V^2 \lim_{r \rightarrow 0^+} \int_0^\infty e^{-rt} \cos(\hat{\epsilon}t) \cos \left[\frac{\lambda_1^2}{\pi} Q_1^{(1)}(t) + \frac{\lambda_2^2}{\pi} Q_1^{(2)}(t) \right] \\ \times e^{-\frac{\lambda_1^2}{\pi} Q_2^{(1)}(t) - \frac{\lambda_2^2}{\pi} Q_2^{(2)}(t)} dt \end{aligned}$$

$Q_{1,2}^{(j)}$ defined as $Q_{1,2}$

Illustration: Recovering the Marcus formula

Consider spectral density

$$J(\omega) \propto \omega^s e^{-\omega/\omega_c}, \quad s > 1 \text{ and } \omega_c > 0$$

and high temperatures, $\omega_c \ll T$. For $1 < s \leq 2$:

$$\gamma_c = \left(\frac{V}{2}\right)^2 \sqrt{\frac{2\pi}{T(\epsilon_{c,1} + \epsilon_{c,2})}} \left(e^{-\frac{(\epsilon - \epsilon_{c,1})^2}{2T(\epsilon_{c,1} + \epsilon_{c,2})}} + e^{-\frac{(\epsilon + \epsilon_{c,2})^2}{2T(\epsilon_{c,1} + \epsilon_{c,2})}} \right)$$

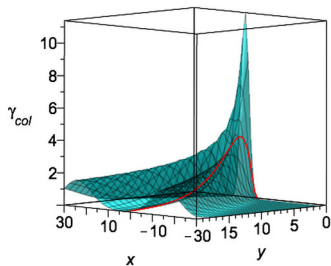
where $\epsilon_{c,j} \propto \lambda_j^2 - \lambda_1 \lambda_2 =$ *reconstruction energies*.

This is “**Generalized Marcus Formula**”; symmetric case $\lambda_1 = -\lambda_2$ reduces to **Marcus Formula** for electron transfer:

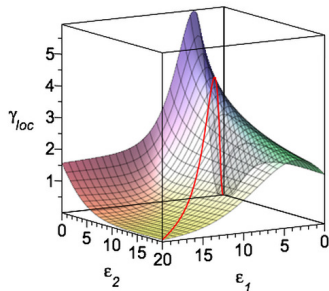
$$\gamma_c = \left(\frac{V}{2}\right)^2 \sqrt{\frac{\pi}{T\epsilon_c}} e^{-\frac{(\epsilon - \epsilon_c)^2}{4T\epsilon_c}} \quad (0 < \epsilon_c \propto \lambda^2)$$

Some numerical results

- Accuracy of generalized Marcus formula:
 - $\omega_c/T \lesssim 0.1$ rates given by the gen. Marcus formula coincide extremely well ($\sim \pm 1\%$) with true values $\gamma_{c,l}$
 - $\omega_c/T \gtrsim 1$ get serious deviations ($\gtrsim 30\%$)
- Asymmetric coupling can significantly increase transfer rate:



Collective: $x \propto \lambda_1^2 - \lambda_2^2$, $y \propto (\lambda_1 - \lambda_2)^2$



Local: $\epsilon_j \propto \lambda_j^2 - \lambda_1 \lambda_2$

Surfaces = $\gamma_{c,l}$

Red curve = symmetric coupling

DECOHERENCE



Result: **Non-interacting dimer** $V = 0$

Populations constant in time and

$$[\rho_S(t)]_{12} = e^{-it\hat{\epsilon}} \mathcal{D}(t) [\rho_S(0)]_{12}$$

- $\lim_{t \rightarrow \infty} [\rho_S(t)]_{12} = 0$ called *full phase decoherence*
- limit nonzero called *partial phase decoherence*

Full decoherence \iff low frequency modes well coupled to dimer:

Lemma. *Full phase deco.* $\iff J(\omega) \sim \omega^s$ with $s \leq 2$ ($\omega \rightarrow 0$)

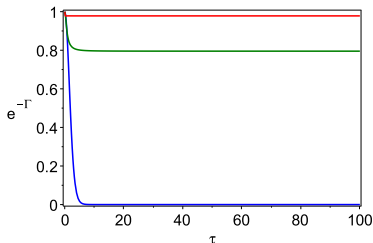
Graph: $\mathcal{D}(t) = e^{-\Gamma(t)}$

$$s = 3$$

Red: $\beta\omega_c = 0.1$

Green: $\beta\omega_c = 1$

Blue: $\beta\omega_c = 5$



Result: Decoherence of the interacting dimer

For $s > 2$: residual asymptotic coherence $\lim_{t \rightarrow \infty} \mathcal{D}(t) = e^{-\Gamma_\infty}$, $\Gamma_\infty > 0$

Theorem (Decoherence) [M. et al, 2016]

Consider the local/collective reservoirs model with λ_1, λ_2 arbitrary. There is a $V_0 > 0$ such that if $0 < |V| < V_0$, then

$$[\rho_S(t)]_{12} = e^{-\Gamma_\infty} e^{-\gamma t/2} e^{-it(\hat{\epsilon} + x_{\text{LS}})} [\rho_S(0)]_{12} + O(V) + O\left(\frac{1}{1+t}\right),$$

where γ is the relaxation rate, $x_{\text{LS}} \in \mathbb{R}$ is the Lamb shift.

- Well-known relation from weak coupling theory (Bloch-Redfield) holds for *all* coupling strengths:

$$\gamma_{\text{decoherence}} = \gamma_{\text{relaxation}}/2$$

- Theorem holds for $s \geq 3$: regime of partial deco., $\Gamma_\infty < \infty$
- We expect to get rigorous result for $s > 1$. But if $s \leq 2$: $\Gamma_\infty = \infty$, above expansion not useful, analysis needs modification

Outline of mathematical method

- Original Hamiltonian

$$H = \frac{1}{2} \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix} + H_R + \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \otimes \phi(\mathbf{g})$$

- 'Unperturbed' case $V = 0$ can be solved explicitly, for **any** values of $\lambda_1, \lambda_2 \in \mathbb{R}$.

Method: **polaron transformation**

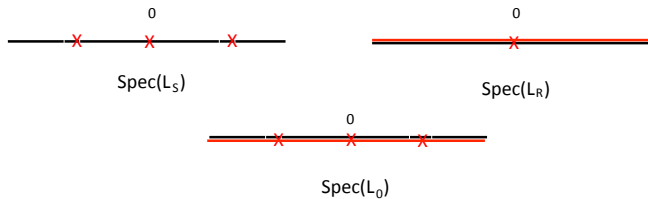
$$U = \exp \{ iP_+ \otimes \phi(\lambda_1 \mathbf{g}/i\omega) + iP_- \otimes \phi(\lambda_2 \mathbf{g}/i\omega) \}$$

Then

$$UHU^* = \frac{1}{2} \begin{pmatrix} \epsilon - \alpha_1 & 0 \\ 0 & -\epsilon - \alpha_2 \end{pmatrix} + H_R + \frac{1}{2} V \sigma_+ \otimes e^{i\phi((\lambda_1 - \lambda_2)\mathbf{g}/i\omega)} + \text{h.c.}$$

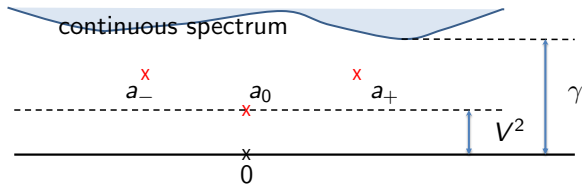
- Approach: link spectral characteristics of H to dynamics. To find spectrum of H , do perturbation theory in V small.

- Since density matrix evolution is $e^{-itH} \rho e^{itH}$, what counts is the *difference* of spectral points of H , i.e., spectrum of *Liouville operator* $L = H \otimes \mathbf{1} - \mathbf{1} \otimes H$



- Eigenvalues of L_0 are embedded in continuous spectrum, so ordinary perturbation theory does not apply (indeed, eigenvalues become complex!)
- Use “complex scaling” or “spectral deformation” or “Mourre theory” to follow eigenvalues into the complex plane as $V \neq 0$

- Basic idea of spectral deformation: $L \mapsto L(\theta)$, $\theta \in \mathbb{C}$ s.t.
 - $L(0) = L$ and $L(\theta)$ is ‘regular’ in θ
 - for increasing $\text{Im}\theta$, the continuous spectrum of $L_0(\theta)$ changes and moves into the complex plane, away from the eigenvalues which do not move. The eigenvalues are then *isolated* points in the spectrum.
- Trade-off: $L(\theta)$ is not self-adjoint any longer.



- Now can do analytic perturbation theory: complex resonances a_j bifurcate out of system Bohr energies $E = 0, \pm\epsilon$

$$a_j = E + V^2 x_{\text{LS}} + iV^2 \gamma + O(V^4)$$

- Then show a diagonalization formula

$$e^{itL(\theta)} = \sum_j e^{ita_j} P_j + O(e^{-\gamma t})$$

Theorem (Resonance expansion) [Könenberg-M. 2016]

Take $\lambda_1, \lambda_2 \in \mathbb{R}$ arbitrary and V small enough. For any initial system-reservoir density matrix ρ_0 , any system observable A , any $t > 0$, we have

$$\mathrm{Tr}(\rho_0 e^{itH} A e^{-itH}) = \langle A \rangle_{\mathrm{SR}, \beta} + \sum_{j=0, \pm} e^{ita_j} \chi_j(A) + O(1/t),$$

where $\langle \cdot \rangle_{\mathrm{SR}}$ is coupled equilibrium, χ_j are linear functionals and a_j are **complex resonance energies** with $\mathrm{Im} a_j \propto V^2 \gamma + O(V^4)$.

Conclusion

- ▶ We consider donor-acceptor type models with
 - small direct donor-acceptor coupling V
 - local or collective noise
- ▶ Using a polaron transformation, we bring the system in a form amenable to perturbation theory in V , *uniformly* in the strength of the coupling with the reservoirs
- ▶ We show a resonance expansion of the dimer dynamics giving the evolution of the reduced density matrix
- ▶ We find the asymptotic state and the relaxation rate (diagonal matrix elements) and the decoherence rate (off-diagonals)
- ▶ For a symmetrically coupled system and high temperatures, we recover the Marcus Formula for relaxation
- ▶ The decoherence rate is half the relaxation rate

Merci de votre attention!