Evolution of a two-level system strongly coupled to a thermal bath

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Collaborations with

M. Könenberg (2016)
G.P. Berman, R.T. Sayre, S. Gnanakaran,
M. Könenberg, A.I. Nesterov and H. Song (2016)

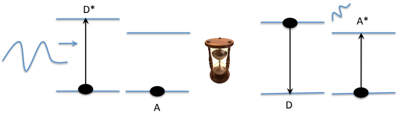
I. A motivation: quantum processes in biology

Excitation transfer process

When a molecule is excited electronically by absorbing a photon, it luminesces by emitting another photon or the excitation is lost in its environment ($\sim$ 1 nanosecond).

Fluorescence

However, when another molecule with similar excitation energy is present within $\sim 1 - 10$ nanometers, the excitation can be swapped between the molecules ($\sim$ 1 picosecond).

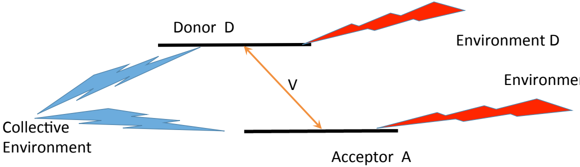


Excitation transfer process: D*+ A$\rightarrow$D + A*

Excitation transfer happens in *biological systems* (chlorophyll molecules during photosynthesis)

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

Processes take place in **noisy environments** (molecular vibrations...)



Collective (correlated) model: D, A have common environment

Excitation transfer process

– Initially the donor is populated
– During the evolution the acceptor population is building up

What is the transfer rate?

Marcus formula for transfer rate (1956)
(Rudolph Marcus, Chemistry Nobel Prize 1992)

$$\gamma_{\mathrm{Marcus}} = \frac{2\pi}{\hbar}|V|^2 \frac{1}{\sqrt{4\pi\,\epsilon_{\mathrm{rec}}\,k_B\,T}} \exp\left[-\frac{(\Delta G + \epsilon_{\mathrm{rec}})^2}{4\,\epsilon_{\mathrm{rec}}\,k_B\,T}\right]$$

V = direct electronic coupling
ϵ_{rec} = reconstruction energy
T = temperature
ΔG = Gibbs free energy change in reaction

Marcus approach and spin-boson model

$$H_{\text{Marcus}} = |R\rangle E_R \langle R| + |P\rangle E_P \langle P| + |R\rangle V \langle P| + |P\rangle V \langle R|$$

R = reactant (donor), P = product (acceptor)
$E_{R,P}$ = energies of collection of classical oscillators

Xu-Schulten '94:

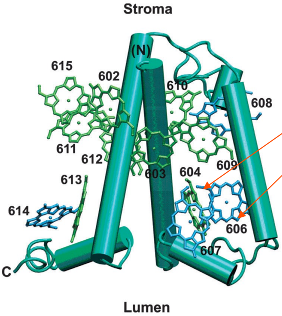
Marcus Hamiltonian is equivalent to spin-boson Hamiltonian

$$H_{\text{SB}} = V\sigma_x + \epsilon\,\sigma_z + H_R + \lambda\sigma_z \otimes \varphi(h)$$

$$\begin{aligned} H_R &= \sum_\alpha \omega_\alpha (a_\alpha^\dagger a_\alpha + 1/2) \\ \varphi(h) &= \tfrac{1}{\sqrt{2}} \sum_\alpha h_\alpha a_\alpha^\dagger + \text{h.c.}, \qquad h_\alpha = \text{form factor} \end{aligned}$$

Towards a structure-based exciton Hamiltonian for the CP29 antenna of photosystem II

Frank Műh, Dominik Lindorfer, Marcel Schmidt am Busch and Thomas Renger, *Phys. Chem. Chem. Phys.*, **16**, 11848 (2014)



Our chlorophyll dimer:

604: Chla, $E^a_{exc} = 14\,827 cm^{-1} = 1.8385 eV$ Acceptor

606: Chlb, $E^b_{exc} = 15\,626 cm^{-1} = 1.9376 eV$ Donor

$$\varepsilon = E^b_{exc} - E^a_{exc} = 99.1 meV$$
$$V = 8.3 meV$$

Our chlorophyll dimer is weakly coupled: $\frac{V}{\varepsilon} \approx 0.08 \ll 1.$

- Relevant parameter regime

– Strong dimer-environment interaction $\lambda^2 \propto \epsilon_{\rm rec} \approx \epsilon$
– Large (physiological) temperatures $k_B T \gg \hbar\omega_c$
– Weakly coupled dimer $V \ll \epsilon$

- Heuristic 'time-dependent perturbation theory' (Leggett '87) $\Rightarrow$

$$\text{“}\ p_{donor} = e^{-\gamma t}\ \text{”}, \qquad \gamma_{\rm Marcus} = \frac{V^2}{4}\sqrt{\frac{\pi}{T\epsilon_{\rm rec}}}\,{\rm e}^{-\frac{(\epsilon-\epsilon_{\rm rec})^2}{4T\epsilon_{\rm rec}}}$$

- The 'usual' *Bloch-Redfield* theory of open quantum systems works for λ small ($\ll \epsilon$), it is *not applicable* here

Our contribution:

1. Develop **rigorous perturbation theory** for dynamics, **valid for all times and any reservoir coupling strength**
2. Prove validity of **exponential decay law** and find **rates of relaxation and decoherence**
3. Establish a **generalized Marcus formula** and extract **scheme for increasing transfer rates and efficiency**

II. Main technical result: Resonance Expansion

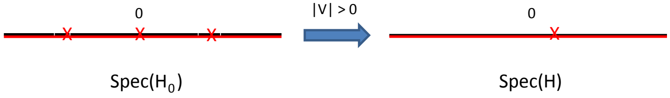
General setup

- Self-adjoint generator of dynamics on Hilbert space $\mathcal{H}$

$$H = H_0 + V\, I$$

  V perturbation parameter, I interaction operator

- Eigenvalues of H_0 are *embedded* in continuous spectrum
- Behaviour of eigenvalues of H_0 under perturbation $V\, I$:
  - *Stable*: Splitting without reduction of total degeneracy
  - *Partially stable*: Splitting **and** reduction of total degeneracy
  - *Unstable*: Disappear for $V \neq 0$



Assumptions

- **Effective coupling** 'Fermi Golden Rule' condition

(Motion of eigenvalues visible to lowest order in perturbation, V^2)

- **Dispersiveness** away from eigenvalues

('Limiting Absorption Principle', regularity of $z \mapsto (H - z)^{-1}$ as $z \to \mathbb{R}$
$\rightsquigarrow$ absolutely continuous spectrum, time-decay)

Theorem [Könenberg-Merkli, 2016]

There is a $V_0 > 0$ *s.t. if* $0 < |V| < V_0$, *then* $\forall t \geq 0$

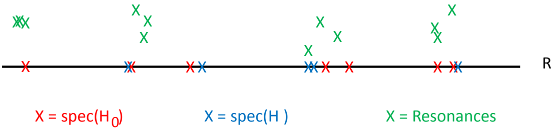
$$\mathrm{e}^{\mathrm{i}tH} = \sum_E \mathrm{e}^{\mathrm{i}tE}\Pi_E + \sum_a \mathrm{e}^{\mathrm{i}ta}\Pi_a + O(1/t)$$

where

$$E \in \mathbb{R}, \qquad \mathrm{Im}\, a \propto V^2 > 0$$

where (E, Π_E) *are* **real** *eigenvalues and eigenprojections of* H *and* (a, Π_a) *are* **complex** *resonance energies and projections. The resonance data have an explicit perturbation expansion in* V.

- Eigenvalues E of H: **oscillation** $\mathrm{e}^{\mathrm{i}tE}$
- Unstable eigenvalues = Resonances: **decay** $|\mathrm{e}^{\mathrm{i}ta}| = \mathrm{e}^{-\gamma V^2 t}$

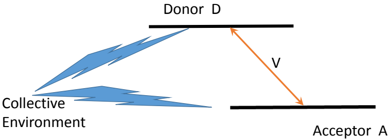


Challenges in proof

- In regime of strong environment coupling the usual (singular) perturbation methods *fail*
- Develop extension of *Mourre theory* for strong coupling regime
- Mourre theory just gives *ergodicity* ('return to equilibrium'), not fine details of dynamics: no decay rates and directions
- We combine *Feshbach-Schur reduction method* and *resolvent representation* of propagator in a new way to obtain our resonance expansion

III. Application: dynamics of a dimer

Donor-acceptor model



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

$$\begin{aligned} H_R &= \int_{\mathbb{R}^3} \omega(k)\, a^*(k) a(k) d^3 k \\ \phi(g) &= \frac{1}{\sqrt{2}} \int_{\mathbb{R}^3} \left(g(k) a^*(k) + \mathrm{adj.} \right) d^3 k \end{aligned}$$

Free bosonic quantum fields

Initial states, reduced dimer state

Intital states unentangled,

$$\rho_{\mathrm{in}} = \rho_S \otimes \rho_R$$

$\rho_S =$ arbitrary, ρ_R reservoir equil. state at temp. $T = 1/\beta > 0$

Reduced dimer density matrix

$$\rho_S(t) = \mathrm{Tr}_{\mathrm{Reservoir}}\left(\mathrm{e}^{-\mathrm{i}tH}\rho_{\mathrm{in}}\mathrm{e}^{\mathrm{i}tH}\right)$$

Dimer site basis $\varphi_1 = \begin{pmatrix}1\\0\end{pmatrix}$ and $\varphi_2 = \begin{pmatrix}0\\1\end{pmatrix}$.

Donor population

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

Relaxation

Theorem (Population dynamics) [M. et al, 2016]
Let λ_D, λ_A be arbitrary. There is a $V_0 > 0$ s.t. for $0 < |V| < V_0$:

$$p(t) = p_\infty + \mathrm{e}^{-\gamma t}\,(p(0) - p_\infty) + O(\tfrac{t}{1+t^2}),$$

where

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

γ = *relaxation rate* $\propto V^2$

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

p_∞ = *equil. value w.r.t. renormalized dimer energies*

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

Properties of final populations

Final donor population (modulo $O(V)$-correction)

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

If *donor strongly coupled* then $\hat{\epsilon} \propto -\lambda_D^2$, so

Increased donor-reservoir coupling increases final donor population

Effect intensifies at lower temperatures

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

Acceptor gets entirely populated if it is strongly coupled to reservoir

Expression for relaxation rate

$$\begin{aligned}\gamma_c &= V^2 \lim_{r\to 0_+} \int_0^\infty \mathrm{e}^{-rt} \cos(\hat{\epsilon}t)\, \cos\left[\frac{(\lambda_D-\lambda_A)^2}{\pi} Q_1(t)\right] \\ &\qquad\qquad \times\ \exp\left[-\frac{(\lambda_D-\lambda_A)^2}{\pi} Q_2(t)\right]\ dt\end{aligned}$$

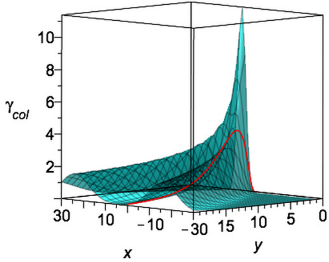
where

$$\begin{aligned}Q_1(t) &= \int_0^\infty \frac{J(\omega)}{\omega^2}\sin(\omega t)\ d\omega, \\ Q_2(t) &= \int_0^\infty \frac{J(\omega)(1-\cos(\omega t))}{\omega^2}\coth(\beta\omega/2)\ d\omega\end{aligned}$$

This is a **Generalized Marcus Formula** – in the symmetric case $\lambda_D = -\lambda_A$ and at high temperatures, $k_B T \gg \hbar\omega_c$, it reduces to the usual Marcus Formula.

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**:



Surface shows γ_c, Red curve = symmetric coupling

$x \propto \lambda_D^2 - \lambda_A^2$, $y \propto (\lambda_D - \lambda_A)^2$

for your attention!