

Effective evolution of open dimers

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ABSTRACT. We analyze the exciton transfer and decoherence processes in a photosynthetic dimer in contact with collective (correlated) and local (uncorrelated) protein-solvent environments. Our approach, based on the framework of the spin-boson model, is mathematically rigorous. We derive explicitly the relaxation and decoherence rates of the exciton transfer process. We establish a generalization of the Marcus formula, yielding the reaction rates for dimer levels which are individually and asymmetrically coupled to environments. Our results hold for arbitrary temperatures and arbitrary strengths of the dimer-environment interaction.

1. Physical Motivation

When a molecule is excited electronically by absorbing a photon, it luminesces by emitting another photon (or the excitation can be lost in a thermal environment). For systems we have in mind, the time scale of this fluorescence is ~ 1 nanosecond.



Fluorescence

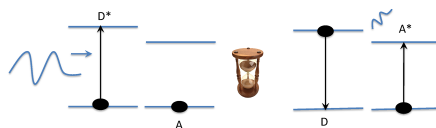
However, when another molecule with similar excitation energy is present within $\sim 1 - 10$ nanometers, the excitation can be swapped between the molecules. This process, called excitation transfer, happens on time-scales of ~ 1 picosecond, about one thousand times faster than fluorescence! An excited ‘donor’ and a non-excited ‘acceptor’ $D^* + A$ transform into a non-excited donor and an excited acceptor $D + A^*$.

This excitation transfer is observed in *biological systems*, notably in chlorophyll molecules during photosynthesis [7]. Similar *charge transfer processes* (electron,

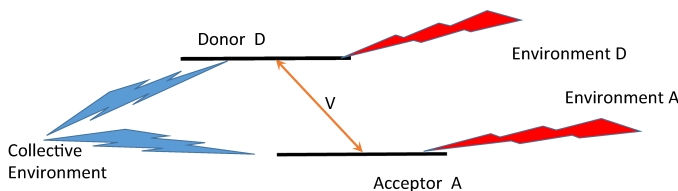
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proton transfer between molecules) happen in chemical (e.g. redox) reactions: $D + A \rightarrow D^- + A^+$, where the donor and acceptor are also called the reactant and product, respectively [5].



The processes in question take place in *noisy environments*, typically thought of as vibrations of surrounding molecules. One can envisage two types of noise interaction. If the donor and acceptor are spatially separated by a distance exceeding the correlation length of the reservoir they are embedded in, then each of D and A may be regarded as interacting with its own, independent reservoir. Otherwise one can model the reservoir as a single one, to which both D and A are coupled.



Local model (right arrows) and collective model (left arrows)
 V : direct exchange interaction

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

Historically, the electronic excitation energy transfer theory is called *Förster theory*, while the charge transfer theory is *Marcus theory*. The main goal of those theories is to predict the *transfer rate*, i.e., the rate at which an initially populated donor depletes by transferring occupation probability to the acceptor. Accordingly, the two theories bring about the rate formulas:

- Förster formula (1948)

$$\gamma_F = \frac{9000 (\ln 10) \kappa^2}{128 \pi^5 N_A \tau_D n_r^4 R^6} \int_0^\infty \frac{f_D(\nu) \epsilon_A(\nu)}{\nu^4} d\nu$$

κ^2 = orientation factor, N_A = Avogadro's number, τ_D = spontaneous decay lifetime of excited donor, n_r = refractive index of medium, R = donor-acceptor distance, $f_D(\nu)$ = normalized donor emission spectrum, $\epsilon_A(\nu)$ = acceptor molar extinction coefficient

- Marcus formula (1956)

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

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

While γ_F and γ_M look very different indeed, they are obtained by the *same* mathematical perturbation theory, simply expressed in different physical parameters.

Marcus based his considerations on a Hamiltonian

$$\begin{aligned} H_{\text{Marcus}} &= |R\rangle E_R \langle R| + |P\rangle E_P \langle P| + |R\rangle V \langle P| + |P\rangle V \langle R| \\ &= \begin{pmatrix} E_R & V \\ V & E_P \end{pmatrix} \end{aligned}$$

where R is the reactant (donor) level and P is the product (acceptor) level, both considered to be quantum states. The (collective) reservoir is taken to consist of classical harmonic degrees of freedom (with the usual notation),

$$\begin{aligned} E_R &= \sum_{\alpha} \left(\frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 q_{\alpha}^2 \right), \\ E_P &= \sum_{\alpha} \left(\frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 (q_{\alpha}^2 - q_{0,\alpha})^2 - \epsilon_{0,\alpha} \right). \end{aligned}$$

In a quantum mechanical treatment, E_R and E_P become *operators* H_R and H_P . It is not surprising that the quantum model can be expressed as the famous *spin-boson system* [4], defined by the Hamiltonian

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

where the $\sigma_{x,z}$ are Pauli matrices and

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

(free bose field). In [10], a dictionary is established, translating the Marcus theory parameters into the spin-boson parameters. In particular, we have $\lambda^2 \propto \epsilon_{\text{rec}}$.

One may then use the heuristic ‘time-dependent perturbation theory’ for the spin-boson model, as given in [4], to obtain the decay law “ $p_{\text{donor}}(t) = e^{-\gamma t}$ ” for the donor population, with a specific relaxation rate γ . Experimental investigations show that for the photosystem we are considering (chlorophyll in light harvesting complexes), the ratio of direct donor-acceptor interaction energy V to donor-acceptor excitation energy difference ϵ is $V/\epsilon \approx 0.1$. This parameter regime is called the *weakly coupled dimer*. If in addition to $V \ll \epsilon$, one considers *high temperatures* $k_B T \gg \hbar \omega_c$ (with ω_c a characteristic ultra-violet cutoff frequency), then the rate γ of Leggett et al. [4] reduces correctly to the *Marcus formula rate*

$$\gamma_{\text{Marcus}} = \frac{V^2}{4} \sqrt{\frac{\pi}{T \epsilon_{\text{rec}}}} e^{-\frac{(\epsilon - \epsilon_{\text{rec}})^2}{4T \epsilon_{\text{rec}}}}.$$

It is also known from experiments that $\epsilon_{\text{rec}} \approx \epsilon$, and since $\epsilon_{\text{rec}} \propto \lambda^2$, we are faced with a system-environment energy of the same order as the Bohr-energy of the system alone. This means that the donor-acceptor pair is *strongly coupled to the reservoir*. We point out that

- Marcus theory is designed to work for large interaction strength with environment (ϵ_{rec}) and for ‘high’ temperatures (room temperature of biological, living systems).

- The ‘usual’ theory of open quantum systems is the *Bloch-Redfield* theory, it is designed for small interactions with the environment and hence does not apply to the situation at hand.

- Rudolph A. Marcus received the 1992 Nobel Prize in Chemistry “for his contributions to the theory of electron transfer reactions in chemical systems” [6].

Our main contributions are:

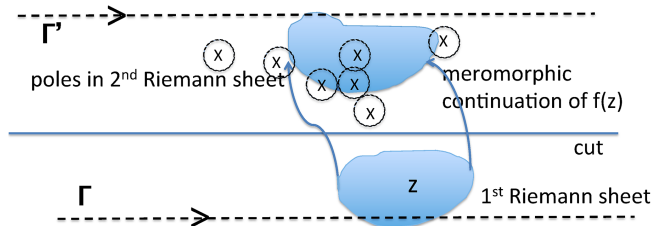
1. We develop a “*dynamical resonance theory*,” a controlled perturbation theory for the dynamics of the weakly coupled dimer ($V \ll \epsilon$), valid for **all times** ($t \geq 0$ arbitrarily large) and **any reservoir coupling strength** ($\lambda \in \mathbb{R}$).

2. We extract from the dynamical resonance theory the precise meaning and the validity of Leggett’s exponential decay law and the rates of relaxation as well as decoherence.

3. We consider individual, possibly different coupling strengths λ_D, λ_A of the donor and acceptor to the environment(s), in contrast to the Marcus case, where $\lambda_D = -\lambda_A$. We then show that an asymmetric coupling can significantly speed up the excitation process.

2. Resonance expansion

Spectral deformation . . . or not! Consider the propagator e^{itL} of a quantum system, where L is the self-adjoint generator (the ‘Liouville operator’, or Hamiltonian). The map $z \mapsto f(z) \equiv \langle \psi, (L - z)^{-1} \phi \rangle$ is analytic in $z \in \mathbb{C}_-$. In the *spectral deformation technique*, one assumes that $f(z)$ has a meromorphic extension, across the cut \mathbb{R} , into \mathbb{C}_+ , with poles lying on the 2nd Riemann sheet. A contour deformation



mation ($\Gamma \rightarrow \Gamma'$) in the usual contour integral expressing the propagator as a line integral over the resolvent then reveals the dynamics as

$$\langle \psi, e^{itL} \phi \rangle = \frac{-1}{2\pi i} \int_{\Gamma} e^{itz} f(z) dz = \sum_{\text{poles } a} e^{ita} f(a) + O(e^{-\alpha t}),$$

where $\alpha > \text{Im} a$ for all poles a (see the picture). Poles a with $\text{Im} a > 0$ then drive temporal decay, while poles $a \in \mathbb{R}$ cause oscillations in time.

How does one construct the meromorphic continuation of f ? Let U_θ , $\theta \in \mathbb{R}$ be a unitary group acting on the Hilbert space of pure states. Then we have

$$f(z) = \langle \psi, (L - z)^{-1} \phi \rangle = \langle \psi_\theta, (L_\theta - z)^{-1} \phi_\theta \rangle,$$

where $L_\theta = U_\theta L U_\theta^*$ and $\psi_\theta = U_\theta \psi$. Suppose now that, under some regularity assumptions, the above right hand side representing $f(z)$ extends meromorphically in the variable θ to some domain of $\theta \in \mathbb{C}$. For $\theta \in \mathbb{C} \setminus \mathbb{R}$ fixed, the operator L_θ is *not*

self-adjoint any longer, and has eigenvalues in \mathbb{C}_+ ('deformed spectrum!'), which are precisely the poles of the function $z \mapsto f(z)$. Then $z \mapsto f(z)$ for $\text{Im}\theta \neq 0$ fixed is the desired meromorphic extension of f . In examples where this scheme is implementable, the eigenvalues of L_θ can be calculated by analytic perturbation theory in some small parameter in L_θ , say the system-environment coupling strength (for $\text{Im}\theta \neq 0$ fixed) and the decay rates are thus explicitly accessible.

So here is the question: What if L_θ does not have a meromorphic extension (due to a lack of some regularity)? Of course, this happens precisely in the kinds of systems of interest here!

- Then we cannot extend to the second Riemann sheet to access the poles.
- How can we recover decay times and directions?

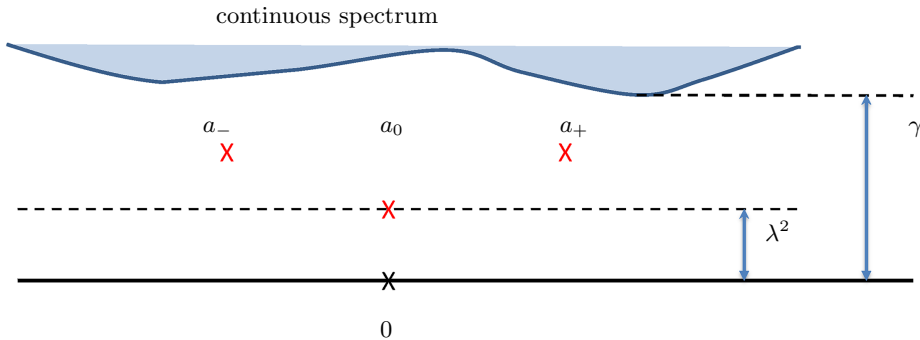
Our task is to develop a method using only a mild regularity condition (as opposed to the existence of a meromorphic continuation), like

$$z \mapsto \langle \psi(L - z)^{-1} \phi \rangle \quad \text{stays bounded as } \text{Im}z \uparrow 0,$$

for a sufficiently rich set of vectors ψ, ϕ , which is called the *limiting absorption principle* (LAP).

2.1. An example where spectral deformation works. The method works for the spin-boson model (with the Hamiltonian H_{SB} given above) at weak coupling (λ small).

- $\lambda = 0$: system and reservoir uncoupled, dynamics factorizes
- $\lambda \neq 0$: $U_\theta =$ spectral translation applies and gives $\text{spec}(L_\theta)$:



Eigenvalues of L_θ are disjoint from the continuous spectrum and one obtains the resonance expansion

$$e^{itL_\theta} = \sum_j e^{ita_j} \Pi_j + O(e^{-\gamma t}).$$

The regularity requirement for this to work is that $\varphi(h)$, the interaction operator between the spin and the bose field, must be 'translation analytic', a condition which is easily satisfied.

2.2. Why the spectral deformation technique fails for the spin-boson model at weak tunneling (V small).

◦ The system (spin) and reservoir (free bose gas) is already interacting in the unperturbed dynamics $V = 0$. One can ‘undo the interaction’ by the unitary *polaron transformation* $U = U(\lambda)$, [3, 4]. Namely,

$$\mathcal{L}_0 \equiv U L_0 U^* = L_S + L_R \quad (\epsilon = 0)$$

◦ When the perturbation $V \neq 0$ is switched on, the transformed Liouville operator becomes

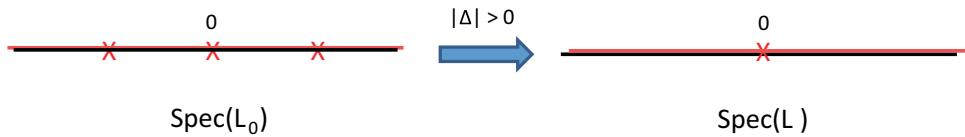
$$\begin{aligned} \mathcal{L} &= \mathcal{L}_0 + V \mathcal{I} \\ \mathcal{I} &= \mathcal{I}(\lambda) = \sigma_+ \otimes W_\beta(\lambda h) + \text{adj.}, \end{aligned}$$

where σ_+ is the spin raising operator and $W_\beta(\lambda h) = e^{i\varphi_\beta(\lambda h)}$ is the thermal Weyl operator.

◦ The perturbation \mathcal{I} is a **bounded operator**, but unfortunately, it **behaves badly under spectral deformation**. Indeed, the spectral deformation of $W_\beta(\lambda h)$ is $\sim e^{V\sqrt{N}}$, where N is the boson number operator. The operator $e^{V\sqrt{N}}$ is ‘hugely unbounded’ and we do not know how to deal with it as a perturbation of \mathcal{L}_0 . This means we do not know how to implement the spectral deformation technique!

However, using *Mourre theory* instead of spectral deformation, one can prove the following result.

Theorem ([3]) $\forall \lambda \in \mathbb{R}$, if $V \neq 0$ is small enough, then \mathcal{L} has absolutely continuous spectrum covering \mathbb{R} and a single simple eigenvalue at the origin. The eigenvector is the coupled equilibrium state Ω .



Two main technical tools in proof of this theorem are:

1. Positive commutator methods, used to show instability of eigenvalues by assuming an effective coupling “*Fermi Golden Rule*” condition.

2. The Limiting Absorption Principle (LAP) to show absolute continuity of the spectrum. Namely, it is well known that if

$$\sup_{x \in (a,b); y > 0} |\langle \psi, (\mathcal{L} - x + iy)^{-1} \psi \rangle| \leq C(\psi)$$

for all ψ in a dense set, then the spectrum of \mathcal{L} in the interval (a, b) is purely absolutely continuous (AC).

The *dynamical consequences of the Theorem* are:

$$\begin{aligned} \mathcal{L} &= 0 \cdot P_\Omega \oplus \bar{\mathcal{L}} P_\Omega^\perp \quad \& \quad \text{spec}(\bar{\mathcal{L}}) \text{ is purely AC, so} \\ e^{it\mathcal{L}} &= P_\Omega \oplus e^{it\bar{\mathcal{L}}} P_\Omega^\perp \quad \longrightarrow \quad P_\Omega, \quad \text{weakly, as } t \rightarrow \infty. \end{aligned}$$

This is rather *incomplete information* compared to the spectral deformation case, where decay rates and directions are obtained as resonance energies and corresponding projections.

How can we recover the full dynamical information

$$e^{it\mathcal{L}} \sim \sum_j e^{ita_j} \Pi_j + \text{remainder}$$

using Mourre theory ?

2.3. Result on Resonance Expansion via Mourre Theory. We consider a family of self-adjoint operators on Hilbert space \mathcal{H} ,

$$L = L_0 + V I, \quad V \in \mathbb{R} \text{ is a perturbation parameter.}$$

The eigenvalues of L_0 are supposed to be embedded in the continuous spectrum of L_0 . An eigenvalue e of L_0 can behave in different ways under perturbation. We call e

- *unstable* if for $V \neq 0$ small, L does not have eigenvalues in a neighbourhood of e
- *partially stable* if for $V \neq 0$ small, L has eigenvalues in a neighbourhood of e with summed multiplicity $< \text{mult}(e)$

We suppose that all eigenvalues of L_0 are either unstable or partially stable with a reduction to dimension one.

If e was an *isolated* eigenvalue of L_0 (which it is not!), with associated spectral projection P_e , then by analytic perturbation theory, the eigenvalues of L near e would be those of the operator

$$eP_e + VP_eIP_e - V^2P_eIP_e^\perp(L_0 - e)^{-1}IP_e + O(V^3).$$

We assume that $P_eIP_e = 0$ for all eigenvalues e of L_0 . Since e is actually an *embedded eigenvalue* of L_0 , the resolvent $P_e^\perp(L_0 - e)^{-1}$ does not exist, but we can expect the 2nd order corrections still to be linked to the **level shift operator**

$$\Lambda_e = -P_eIP_e^\perp(L_0 - e + i0_+)^{-1}IP_e,$$

where $(L_0 - e + i0_+)^{-1} = \lim_{\epsilon \rightarrow 0_+} (L_0 - e + i\epsilon)^{-1}$.

We make an assumption that the instability of eigenvalues is visible at order V^2 in the perturbation already. This assumption on the effectiveness of the coupling is often referred to as the *Fermi Golden Rule Condition*. It is expressed in terms of the level shift operators as follows. We assume that

- (1) The eigenvalues of all the level shift operators Λ_e are simple.
- (2) e unstable \implies all the eigenvalues $\lambda_{e,0}, \dots, \lambda_{e,m_e-1}$ of Λ_e have strictly positive imaginary part.
- (3) e partially stable \implies Λ_e has a single real eigenvalue $\lambda_{e,0}$. All other eigenvalues $\lambda_{e,1}, \dots, \lambda_{e,m_e-1}$ have imaginary part > 0 .

In particular, Λ_e is diagonalizable, so

$$\Lambda_e = \sum_{j=0}^{m_e-1} \lambda_{e,j} P_{e,j},$$

where $P_{e,j}$ are the (rank one) spectral projections.

To state our second main assumption, let P_e denote the eigenprojection associated to eigenvalue e of L_0 and set

$$R_z = (L - z)^{-1} \quad \text{and} \quad R_z^{P_e} = (P_e^\perp L P_e^\perp - z)^{-1} \Big|_{\text{Ran} P_e^\perp}.$$

We assume that the Limiting Absorption Principle holds. Namely, for every eigenvalue e of L_0 ,

$$\sup_{y < 0, x \approx e} |\langle \phi, R_{x+iy}^{P_e} \psi \rangle| \leq C(\phi, \psi) < \infty$$

and

$$\sup_{y < 0, x \text{ away from all } e} |\langle \phi, R_{x+iy} \psi \rangle| \leq C(\phi, \psi) < \infty$$

for all vectors ϕ, ψ in a dense set \mathcal{D} .

Denote by Π_{E_e} the spectral projection of L associated to the eigenvalue E_e (near e). Then we have the following result.

Theorem (Resonance expansion, [2]) $\exists V_0 > 0$ s.t. if $0 < |V| < V_0$ then $\forall t > 0$,

$$\begin{aligned} e^{itL} &= \sum_{e \text{ partially stable}} \left\{ e^{itE_e} \Pi_{E_e} + \sum_{j=1}^{m_e-1} e^{it(e+V^2 a_{e,j})} \Pi'_{e,j} \right\} \\ &+ \sum_{e \text{ unstable}} \sum_{j=0}^{m_e-1} e^{it(e+V^2 a_{e,j})} \Pi'_{e,j} + O(1/t) \end{aligned}$$

(weakly on \mathcal{D}). The exponents $a_{e,j}$ and the operators $\Pi'_{e,j}$ are close to the spectral data of the level shift operator Λ_e , namely,

$$a_{e,j} = \lambda_{e,j} + O(V), \quad \Pi'_{e,j} = P_{e,j} + O(V).$$

3. Application: dynamics of a dimer

We present results for the collective environment model,

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

$$H_R = \int_{\mathbb{R}^3} \omega(k) a^*(k) a(k) d^3 k$$

$$\phi(g) = \frac{1}{\sqrt{2}} \int_{\mathbb{R}^3} (g(k) a^*(k) + \text{adj.}) d^3 k,$$

the reservoir being a free bosonic quantum field. We take the initial state to be disentangled,

$$\rho_{\text{in}} = \rho_S \otimes \rho_R,$$

where ρ_S is an arbitrary dimer (two-level) density matrix and ρ_R is the reservoir equilibrium state at temperature $T = 1/\beta > 0$. The reduced dimer density matrix is

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

and we denote the dimer site basis by $\varphi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\varphi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. The donor population is given by

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

The evolution $t \mapsto p(t)$ is called the *relaxation* dynamics while *decoherence* is the evolution of the off-diagonal matrix element

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

3.1. Dynamics for $V = 0$.

- The populations (diagonal of density matrix) are constant in time, since H_S commutes with the interaction operator.
- The total system has a 2-dimensional manifold of stationary states and one equilibrium (KMS) state given by

$$\rho_{\beta, \lambda} = \frac{e^{-\frac{\beta}{2}(\epsilon - \alpha_D)}}{Z_{\text{ren}}} |\varphi_1\rangle\langle\varphi_1| \otimes \rho_{R,1} + \frac{e^{-\frac{\beta}{2}(-\epsilon - \alpha_A)}}{Z_{\text{ren}}} |\varphi_2\rangle\langle\varphi_2| \otimes \rho_{R,2},$$

where the *effective energy shifts* $\alpha_{D,A}$ are $\propto \lambda_{D,A}^2$ and $\rho_{R,j}$ are two explicit reservoir states.

- The reduced dimer equilibrium state equals

$$\rho_{\text{ren}} = \text{Tr}_R \rho_{\beta, \lambda} = \frac{e^{-\beta H_{\text{ren}}}}{Z_{\text{ren}}}, \quad H_{\text{ren}} = \frac{1}{2} \begin{pmatrix} \epsilon - \alpha_D & 0 \\ 0 & -\epsilon - \alpha_A \end{pmatrix}$$

- We will show that for $V \neq 0$ (small), the total system has a unique stationary state (=KMS) and all initial states converge to it as $t \rightarrow \infty$.

3.2. Dynamics for $V \neq 0$. An important quantity is the *reservoir spectral function*, defined by

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

where $\widehat{\mathcal{C}}(\omega)$ is the Fourier transform of reservoir correlation function. Reservoir effects are encoded in $J(\omega)$ and our mathematical theory requires the **regularity conditions**

$$\begin{aligned} J(\omega) &\sim \omega^s && \text{with } s \geq 3 \text{ as } \omega \rightarrow 0 \\ J(\omega) &\sim \omega^{-\sigma} && \text{with } \sigma > 3/2 \text{ as } \omega \rightarrow \infty. \end{aligned}$$

We point out that a minimal ‘*priori*’ condition is $s > 1$ (super-ohmic), but the range $1 < s < 3$ is not treatable up to now with our (or any other rigorous) method. This minimal condition is needed to guarantee that the polaron transformation can be applied to the Hamiltonian, which is the starting point of our analysis for strong system-environment couplings.

Theorem (Population dynamics, relaxation [8]) *Consider the local or collective reservoirs model. Let λ_D, λ_A be arbitrary. There is a $V_0 > 0$ s.t. for $0 < |V| < V_0$:*

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

where

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

and γ is the relaxation rate $\propto V^2$ (taking different values for the local and collective reservoir cases), $\alpha_{D,A}$ are renormalizations of the unperturbed dimer energies $\pm\epsilon$ ($\propto \lambda_{D,A}^2$) and p_∞ is the equilibrium value w.r.t. renormalized dimer energies.

Notes: (1) The remainder in the above expression for $p(t)$ is small on a time-scale $\gamma t \ll 1$, i.e., $t \ll V^{-2}$.

(2) The time-asymptotics is resolved correctly: as $t \rightarrow \infty$, $p(t)$ approaches its true value p_∞ . It is possible to construct a perturbation theory giving the expansion $p(t) = p_\infty + e^{-\gamma t}(p(0) - p_\infty) + O(V)$, with a remainder small in V and uniform in time, but not decaying in time. This needs a slight modification of the proofs in [2].

3.3. Properties of final populations. The final donor population (modulo $O(V)$ -correction) is given by

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

where $\hat{\epsilon} := \epsilon - \frac{\alpha_D - \alpha_A}{2}$ is the effective energy gap. If the donor is strongly coupled ($\lambda_D^2 \gg \max\{\lambda_A^2, \epsilon\}$) then $\hat{\epsilon} \propto -\lambda_D^2$, and so we have the following fact: *Increased donor-reservoir coupling increases final donor population.* This effect intensifies at lower temperatures,

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

We conclude that *the acceptor gets entirely populated if it is strongly coupled to reservoir*, yielding a good process efficiency.

3.4. Expression for relaxation rate. The rate γ (for the collective reservoir model) is given by

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

where

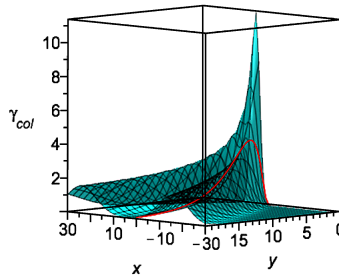
$$\begin{aligned} Q_1(t) &= \int_0^\infty \frac{J(\omega)}{\omega^2} \sin(\omega t) d\omega, \\ Q_2(t) &= \int_0^\infty \frac{J(\omega)(1 - \cos(\omega t))}{\omega^2} \coth(\beta\omega/2) d\omega \end{aligned}$$

This expression for γ 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

$$\gamma_{\text{Marcus}} = \left(\frac{V}{2} \right)^2 \sqrt{\frac{\pi}{T\epsilon_{\text{rec}}}} e^{-\frac{(\epsilon - \epsilon_{\text{rec}})^2}{4T\epsilon_{\text{rec}}}} \quad (0 < \epsilon_{\text{rec}} \propto \lambda^2).$$

3.5. Some numerical results.

- Accuracy of generalized Marcus formula:
 - For ω_c/T less than about 0.1, the numerics show that the rates given by the generalized Marcus formula coincide extremely well ($\sim \pm 1\%$) with the true value, γ given by the formula above. As the temperature decreases, the Marcus formula is not applicable any more (it is only the high-temperature limit of the true value for the relaxation rate).
 - For ω_c/T larger than about 1, the numerics show serious deviations ($\sim 30\%$) between the Marcus formula and the true value.
- An asymmetric coupling can *significantly increase the transfer rate*:



The surface shows the (true) collective relaxation rate $\gamma \equiv \gamma_{col}$ versus the parameters $x \propto \lambda_D^2 - \lambda_A^2$ and $y \propto (\lambda_D - \lambda_A)^2$. The curve (red color in online version) on the surface corresponds to the usual Marcus formula, where $\lambda_A = -\lambda_D$. We see from the graph that a significant increase in γ can be achieved for a suitable asymmetric coupling, $\lambda_D \neq \lambda_A$.

3.6. Decoherence of the dimer. For the non-interacting dimer ($V = 0$), the populations are constant in time and the off-diagonal matrix element evolves as

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

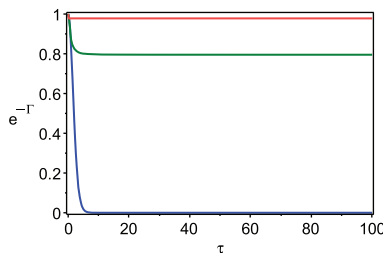
If $\lim_{t \rightarrow \infty} [\rho_S(t)]_{12} = 0$ we say the dimer undergoes *full phase decoherence*. If that limit is not zero, we say it undergoes *partial phase decoherence*. One can show that the low frequency modes of the reservoir are responsible for full decoherence. Namely, we have full decoherence if and only if the low frequency modes are ‘well coupled’ to the dimer, as the following results explains.

Lemma ([8]) *Suppose the reservoir spectral function has the form $J(\omega) \sim \omega^s$ for ω small. Then the dimer exhibits full phase decoherence if and only if $s \leq 2$.*

The following graph shows the decoherence function $\mathcal{D}(t)$ as a function of the (rescaled) time, for different values of the temperature.

Graph: $\mathcal{D}(t) = e^{-\Gamma(t)}$ for $s = 3$

- Top curve: $\beta\omega_c = 0.1$
- Middle curve: $\beta\omega_c = 1$
- Bottom curve: $\beta\omega_c = 5$



We see that the higher the temperature (i.e., the smaller β), the *lower* the degree of long-time decoherence. This can be explained by the fact that at higher temperatures, the proportion of low energy modes in the reservoir is smaller than at lower temperatures. Then, since decoherence is driven significantly by low frequency modes (see the Lemma), less decoherence results at high temperatures.

Decoherence of the interacting dimer

For $s > 2$, we have residual asymptotic coherence, namely $\lim_{t \rightarrow \infty} \mathcal{D}(t) = e^{-\Gamma_\infty} > 0$. The following result examines the decay to the final coherences.

Theorem (Decoherence, [8]) *Consider the local or collective reservoirs model with λ_D, λ_A arbitrary and $s \geq 3$. There is a $V_0 > 0$ such that if $0 < |V| < V_0$, then*

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

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

Notes. (1) The theorem shows that the following well-known relation from weak coupling theory (Bloch-Redfield) holds for *all* coupling strengths:

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

(2) The theorem holds for $s \geq 3$, which is in the regime of partial decoherence, where $\Gamma_\infty < \infty$. We expect to get a rigorous result in the larger region $s > 1$. But for $s \leq 2$ we will have $\Gamma_\infty = \infty$ (Lemma above!) and so the above expansion not useful. Our analysis needs then to be modified.

4. Outline of the proof of the resonance expansion

We have a self-adjoint operator L_0 which is perturbed into $L_0 + V I$ s.t.

- all eigenvalues of L_0 are embedded
- all eigenvalues of L_0 are either unstable or reduce to dimension one under perturbation
- the Limiting Absorption Principle holds

We want to show an expansion

$$\begin{aligned} e^{itL} &= \sum_{e \text{ part. stable}} \left\{ e^{itE_e} \Pi_{E_e} + \sum_{j=1}^{m_e-1} e^{it(e+V^2 a_{e,j})} \Pi'_{e,j} \right\} \\ &+ \sum_{e \text{ unstable}} \sum_{j=0}^{m_e-1} e^{it(e+V^2 a_{e,j})} \Pi'_{e,j} + O(1/t), \end{aligned}$$

in which the resonance data $a_{e,j}, \Pi'_{e,j}$ are obtained by perturbation theory in V .

Decomposing the resolvent using the Feshbach map. Let P_e be the spectral projection associated to the eigenvalue e of L_0 . According to the Feshbach map decomposition [2, 3], the resolvent $(L - z)^{-1}$ can be written as

$$R_z \equiv (L - z)^{-1} = F_z^{-1} + \bar{R}_z + B_z,$$

where

$$\begin{aligned} F_z &:= P_e(e - z - V^2 I \bar{R}_z I) P_e \\ \bar{R}_z &:= (P_e^\perp L P_e^\perp - z)^{-1} \Big|_{\text{Ran} P_e^\perp} \\ B_z &= -V F_z^{-1} I \bar{R}_z - V \bar{R}_z I F_z^{-1} + V^2 \bar{R}_z I F_z^{-1} I \bar{R}_z \end{aligned}$$

The operator F_z^{-1} is finite-dimensional. It acts on $\text{Ran} P_e$. The operator \bar{R}_z ‘is dispersive’, namely a LAP holds for it, away from the eigenvalues of L_0 . This implies purely AC spectrum of L and hence time-decay in the propagation it generates. The operator B_z is of higher order in V and is dispersive as well.

By the standard resolvent representation of the propagator, we have (for any $w > 0$ [and we will take $w \rightarrow 0_+$])

$$e^{itL}\psi = \frac{-1}{2\pi i} \int_{\mathbb{R}-iw} e^{itz} R_z \psi dz$$

We now subdivide the integration into regions close to e and away from e . For the purpose of the present exposition, let us focus on a partially stable eigenvalue e of L_0 and assume $e = 0$ and that L has a single, simple eigenvalue $E = 0$ (no shift) for small V . Let J be interval around 0 (containing no eigenvalue of L_0 but 0). The contribution to $\langle \varphi, e^{itL}\psi \rangle$ from the integral over J is

$$\int_{J-iw} e^{itz} \langle \varphi, R_z \psi \rangle dz = \int_{J-iw} e^{itz} [\langle \varphi, F_z^{-1} \psi \rangle + \langle \varphi, \bar{R}_z \psi \rangle + \langle \varphi, B_z \psi \rangle] dz$$

(A) *Contribution of F_z^{-1} .* Set $P \equiv P_0$ (here $e = 0$). The Feshbach map equals

$$F_z = P(-z - V^2 I \bar{R}_z I) P \equiv -z + V^2 A_z, \quad z \in \mathbb{C}_-$$

defining the operator A_z . The latter can be diagonalized,

$$A_z = \sum_{j=0}^{d-1} a_j(z) Q_j(z) \quad \text{so that} \quad F_z^{-1} = \sum_{j=0}^{d-1} \frac{Q_j(z)}{-z + V^2 a_j(z)}.$$

Therefore,

$$\int_{J-iw} e^{itz} \langle \varphi, F_z^{-1} \psi \rangle dz = \sum_{j=0}^{d-1} \int_{J-iw} \frac{e^{itz}}{-z + V^2 a_j(z)} \langle \varphi, Q_j(z) \psi \rangle dz$$

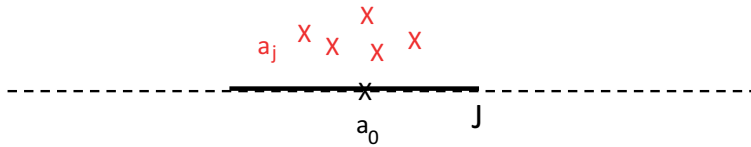
Now A_z is approximately the level shift operator Λ_0 , namely

$$A_z = -PI(\bar{L} - z)^{-1}IP = \underbrace{-PI(\bar{L}_0 + i0_+)^{-1}IP}_{\text{Level Shift Operator } \Lambda_0} + O(V) + O(z).$$

Therefore, the eigenvalues a_j of A_z are approximately the eigenvalues λ_j of Λ_0 , namely

$$\begin{aligned} a_j(z) &= \lambda_j + O(V) + O(z), \quad j = 1, \dots, d-1 \\ a_0(z) &= O(z) \end{aligned}$$

(L has a simple eigenvalue at 0, which by the ‘isospectrality of Feshbach map’ implies that $a_0(0) = 0$ for all V .)



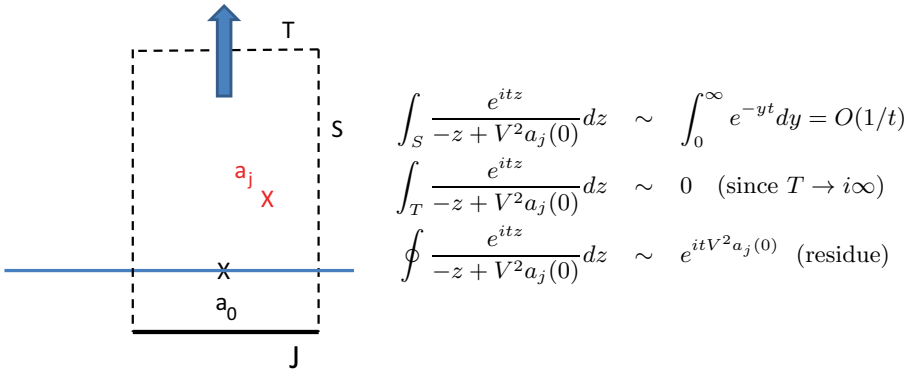
The resonances $a_0 \in \mathbb{R}$ and a_j with $\text{Im} a_j > 0$ close to the interval J .

We thus obtain

$$\int_{J-iw} e^{itz} \langle \varphi, F_z^{-1} \psi \rangle dz = \sum_{j=0}^{d-1} \int_{J-iw} \frac{e^{itz}}{-z + V^2 a_j(z)} \langle \varphi, Q_j(z) \psi \rangle dz$$

$$\approx \sum_{j=0}^{d-1} \langle \varphi, Q_j(0) \psi \rangle \int_{J-iw} \frac{e^{itz}}{-z + V^2 a_j(0)} dz$$

where the approximation is for small intervals J around zero. To estimate the last integral in the summand above, we use standard complex analysis. Namely, we complete the line integral into one over a closed contour as depicted in the diagram below, adding two sides S and a top T (which will be moved to $i\infty$). The integrals over the parts of the contour are easily estimated as indicated:



It follows that

$$\frac{1}{2\pi i} \int_{J-iw} e^{itz} \langle \varphi, F_z^{-1} \psi \rangle dz = \langle \varphi, Q_0(0) \psi \rangle + \sum_{j=1}^{d-1} e^{itV^2 a_j(0)} \langle \varphi, Q_j(0) \psi \rangle + O(1/t).$$

To analyze the part which is constant in time on the right side, we notice that the spectral projection of L for the (embedded) eigenvalue 0 is

$$\Pi_0 = \lim_{V \rightarrow 0^+} (iV)(L - 0 + iV)^{-1}.$$

Then, using the Feshbach decomposition of the resolvent, one identifies

$$\langle \varphi, Q_0(0) \psi \rangle = \langle \varphi, \Pi_0 \psi \rangle + O(V).$$

The contributions coming from B_z will add up precisely to give the remainder term $O(V)$ on the right side. The decaying parts reveal a rate given by the “Fermi Golden Rule”,

$$e^{itV^2 a_j(0)} = e^{itV^2 [\lambda_j + O(V)]}.$$

(B) *Contributions of B_z and \bar{R}_z .* We use the LAP for \bar{R}_z to show that

$$\sup_{z \in \mathbb{C}_-} \left| \frac{d}{dz} \langle \varphi, \bar{R}_z \psi \rangle \right| \leq C,$$

then we integrate by parts w.r.t. z and obtain

$$\int_{J-iw} e^{itz} \langle \varphi, \bar{R}_z \psi \rangle dz = O(1/t).$$

To treat

$$\int_{J-iw} e^{itz} \langle \varphi, B_z \psi \rangle dz$$

where $B_z = -VF_z^{-1}I\bar{R}_z - V\bar{R}_zIF_z^{-1} + V^2\bar{R}_zIF_z^{-1}I\bar{R}_z$, we use again the spectral representation of F_z^{-1} and get *corrections* (to all orders in V) of the contributions coming from F_z^{-1} explained above.

Summary

- We develop a resonance expansion for the dynamics of a dimer strongly coupled to reservoirs. The expansion is valid for arbitrarily large dimer-reservoir interactions and for all times $t \geq 0$.

- Since analytic spectral deformation theory does not apply to the systems in question (due to the large coupling), we develop a Mourre theory which allows to treat ‘singular perturbations’ (strong coupling) and we extract from it decay times and directions. This is our main technical novelty, given in [2]. The only work we are aware of, which is similar in spirit to ours, is [1]. But the method developed there is valid only for zero temperature systems and weak coupling between the system and environment.

- We establish a generalized Marcus formula for donor-acceptor reaction rates, uncovering new physical properties (e.g. population values), not visible in the previous, usual formula, [8].

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