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# The mathematics of quantum transfer processes in biological systems

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Quantum donor-acceptor ($D$-$A$) systems are basic models for the transfer of matter, energy and charge. In quantum chemistry, they are used to study electrons jumping from a donor to an acceptor chemical species. Canadian chemist Rudolf Marcus was awarded the Nobel Prize in 1992 for his theory explaining energy transfer reactions [4, 5]. More recently it was realized that similar mechanisms are at the core of processes in biological systems, specifically in photosynthesis in plants and bacteria. While classical models are not able to render correct predictions for the experimentally established data in photosynthetic processes, quantum models are [7]. A plant or bacterium captures a sunlight photon, which energetically excites a chlorophyll molecule electron. This excitation is then transferred, extraordinarily quickly and virtually without loss, along a chain of donor and acceptor chlorophyll molecules, until it reaches a reaction centre where the excitation facilitates slower chemical reactions.

Crucially, $D$-$A$ systems interact with surrounding molecules and are thus *open* (not isolated). The 'noisy' surrounding environment is typically modeled by a collection of many oscillatory degrees of freedom. The paradigmatic such open model is the spin-boson system [3], which describes a two level quantum system (spin) interacting with a quantum field (free bosonic degrees of freedom). Interpreting the two levels as the excited states of a donor and an acceptor, the spin-boson model suitably describes the open $D$-$A$ system. The $D$ and $A$ are occupied (host the excitation) with probabilities $p_D \in [0,1]$ and $p_A = 1 - p_D$, respectively. Of key interest is the time evolution of the donor probability, $p_D(t)$, *e.g.* knowing that $D$ is initially fully occupied (has captured a photon) and that the quantum field is in equilibrium at a given (say, room) temperature. According to the postulates of quantum theory,

$$p_D(t) = \langle \mathrm{e}^{-\mathrm{i}tL}\Psi_0, P\mathrm{e}^{-\mathrm{i}tL}\Psi_0\rangle. \tag{1}$$

Here, $\langle\cdot,\cdot\rangle$ is the inner product of the Hilbert space $\mathcal{H}$ describing the whole system and $\Psi_0 \in \mathcal{H}$, $\|\Psi_0\| = 1$, is the initial state of $D$-$A$ plus environment. As prescribed by the Schrödinger equation, the state at time $t$ is $\mathrm{e}^{-\mathrm{i}tL}\Psi_0$, where $\mathbb{R} \ni t \mapsto \mathrm{e}^{-\mathrm{i}tL}$ is a unitary group on $\mathcal{H}$, generated by a selfadjoint $L$, called the Liouvillian. $P$ in (1) is an orthogonal projection, playing the role of the 'observable' corresponding to the donor probability (other physical quantities correspond to other operators). The concrete form of $\mathcal{H}, L$ and $P$ are well known for the open $D$-$A$ system.[1] There are two 'coupling constants' in $L$: $\Delta \geq 0$ measures the the strength of the direct (*e.g.* 'dipole-dipole') interaction between $D$ and $A$ while $\lambda \geq 0$ measures that of $D$-$A$ with the environment. The values of these parameters are known from experiments and in the biological systems of interest, the environment coupling is strong, $\lambda \gg \Delta$. Accordingly, one is led to decompose the Liouvillian as

$$L = L_0(\lambda) + \Delta I, \tag{2}$$

where the 'unperturbed operator' $L_0(\lambda)$ generates the dynamics for the $D$-$A$ *already coupled to the environment* ($\lambda \neq 0$), and the operator $I$ describes the direct interaction between $D$ and A. Usually in open systems, perturbation theory is done in small couplings to the environment, the unperturbed case being simply the *uncoupled* system and environment. Here though, it must be done in the internal system parameter $\Delta$ and the unperturbed case is the $D$-$A$ already interacting with the environment. Nevertheless, using a 'polaron transformation' one can solve the dynamical problem for $L_0(\lambda)$ exactly, so (2) is suitable for a perturbation theory in $\Delta$. However, in the strongly coupled situation at hand, $L$ lacks sufficient 'regularity' for standard methods (spectral deformations, standard Mourre theory) from the spectral analysis of Liouvillians to apply. Still, it is possible to develop a 'singular Mourre theory' to deal with this case [1, 2]. The main result is an expansion of the propagator $\mathrm{e}^{\mathrm{i}tL}$ for a class of operators $L$ including Liouvillians as described above. The expansion exhibits oscillatory and decaying (in time) directions of the dynamics in Hilbert space.

**Expansion of the propagator.** Let $L = L_0 + \Delta I$ be a selfadjoint operator on a Hilbert space $\mathcal{H}$, such that the selfadjoint $L_0$ has eigenvalues $e$, with multiplicities $m_e$, embedded in continuous spectrum. As $\Delta \neq 0$, every $e$ is either unstable ($L$ does not have any eigenvalues close to $e$, as $\Delta \neq 0$), or it bifurcates into a group of ($\leq m_e$) real eigenvalues. In the latter case we say $e$ is partially stable and we assume here for simplicity that partially stable $e$ undergo a reduction to dimension one, denoting by $E_e = e + O(\Delta) \in \mathbb{R}$ the associated eigenvalue of $L$. Under the assumptions that **(1)** the first order perturbation terms vanish

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[1] We are dealing with a spatially infinitely extended reservoir in thermal equilibrium, and so the Gelfand-Naimark-Segal construction of the thermal Weyl $C^*$-algebra is used to find the Hilbert space representation. The Liouvillian is not unique and one takes advantage of the Tomita-Takesaki theory of von Neumann algebras to construct a version of $L$ suitable for the further analysis.

$P_e I P_e = 0$ ($P_e$ being the spectral projection of $L_0$ associated to $e$), **(2)** the (formal) second order perturbation terms are non-degenerate (Fermi Golden Rule Condition) and **(3)** the reduced resolvent maps $\mathbb{C}_- \ni z \mapsto (P_e^\perp L P_e^\perp - z)^{-1} \restriction_{\mathrm{Ran} P_e^\perp}$ are sufficiently regular for $\mathrm{Re} z$ close to $e$ (Limiting Absorption Principle), we show the following result in [2].

$\exists c > 0$ s.t. for $0 < |\Delta| < c$ and all $t > 0$, we have, weakly on a dense set of vectors in $\mathcal{H}$,

$$\begin{aligned} \mathrm{e}^{\mathrm{i}tL} = \sum_{\substack{\text{partially}\\ \text{stable } \mathrm{e}}} \Big\{ \mathrm{e}^{\mathrm{i}tE_e} \Pi_{E_e} + \sum_{j=1}^{m_e-1} \mathrm{e}^{\mathrm{i}t(e+\Delta^2 a_{e,j})} \Pi'_{e,j} \Big\} \\ + \sum_{\substack{\text{unstable}\\ e}} \sum_{j=0}^{m_e-1} \mathrm{e}^{\mathrm{i}t(e+\Delta^2 a_{e,j})} \Pi'_{e,j} + O(1/t) \end{aligned} \tag{3}$$

Here, $\Pi_{E_e}$ is the spectral projection of $L$ associated to the eigenvalue $E_e$. The exponents satisfy $a_{e,j} = \lambda_{e,j} + O(\Delta)$ with $\mathrm{Im}\lambda_{e,j} > 0$ (implying time decay) and $\Pi'_{e,j} = P_{e,j} + O(\Delta)$ are projection operators (decay directions). The first sum shows oscillatory parts $\propto \mathrm{e}^{\mathrm{i}tE_e}$ of the surviving partially stable eigenvalues and decaying parts due to the loss of multiplicity, while the second sum, associated to unstable eigenvalues, is purely decaying. The $\Delta$ independent $\lambda_{e,j}$ and $P_{e,j}$ can be calculated by perturbation theory. The decaying exponentials stay sizable for long times $t \lessapprox (\Delta^2 \ \mathrm{Im}\lambda_{e,j})^{-1}$ over which the $O(1/t)$ remainder is subdominant ($t$ not too small).

**Application to transfer processes.** The expansion (3) can be used to analyze the time evolution of the donor probability $p_D(t)$, (1), in the setting $\lambda \gg \Delta$ encountered in biological applications. We find [6]

$$p_D(t) = p_\infty + \mathrm{e}^{-\gamma t}\,(p(0) - p_\infty) + O(1/t) \tag{4}$$

Here $p_\infty$ is the asymptotic (renormalized by strong interaction) thermal equilibrium value and

$$\begin{aligned} \gamma = \Delta^2 \lim_{r \to 0_+} \int_0^\infty \mathrm{e}^{-rt} \cos(\epsilon t) \\ \cos\left(\lambda^2 Q_1(t)\right) \mathrm{e}^{-\lambda^2 Q_2(t)}\ dt + O(\Delta^4) \end{aligned} \tag{5}$$

where $\epsilon$ is the (renormalized) $D$-$A$ energy difference and the $Q_{1,2}(t)$ are quantities depending only on the quantum field (spectral density function, temperature). The result (4), (5) is valid for $\Delta$ small enough but *for all* $\lambda \in \mathbb{R},\ t > 0.$ In the high temperature regime $T \gg \hbar\omega_c$ (a cutoff frequency) the relaxation rate $\gamma$ becomes (to leading order)

$$\gamma_{\mathrm{M}} = \left(\frac{\Delta}{2}\right)^2 \sqrt{\frac{\pi}{T\epsilon_r}}\,\mathrm{e}^{-\frac{(\epsilon-\epsilon_r)^2}{4T\epsilon_r}} \tag{6}$$

where $\epsilon_r$ is an (explicit) constant, called the reorganization energy. Relation (6) is the famous *Marcus formula* for the transition rate. We now have a *proof* of the Marcus formula.[2] Of course, the expansion (3) can be used to analyze *any* $D$-$A$ observable (and even reservoir observables), not just the donor probability. The current setup also allows for various generalizations of the model which alter the speed and efficiency of the reaction, as discussed in [6].

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[2] This is the only proof we are aware of and it assumes a suitable infrared and ultraviolet behaviour of the coupling functions. Marcus' arguments are heuristic and so is the Fermi Golden Rule type calculation for $\gamma$ given by Leggett and collaborators [3].