Dynamics of a Chlorophyll Dimer in Collective and Local Thermal Environments

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Abstract

We present a theoretical analysis of exciton transfer and decoherence effects in a photosynthetic dimer interacting with collective (correlated) and local (uncorrelated) protein-solvent environments. Our approach is based on the framework of the spin-boson model. We derive explicitly the thermal relaxation and decoherence rates of the exciton transfer process, valid for arbitrary temperatures and for arbitrary (in particular, large) interaction constants between the dimer and the environments. We establish a generalization of the Marcus formula, giving reaction rates for dimer levels possibly individually and asymmetrically coupled to environments. We identify rigorously parameter regimes for the validity of the generalized Marcus formula. The existence of long living quantum coherences at ambient temperatures emerges naturally from our approach.

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1 Introduction

When a sunlight photon is absorbed by a light-sensitive molecule (such as chlorophyll or carotenoid) in a light-harvesting photosynthetic complex (LHC), the photon energy is stored in the molecule in the form of an exciton, an excited electron state of the molecule. The exciton then travels very quickly (some picoseconds) inside the LHC and reaches the reaction center (RC), where charge separation, and afterwards relatively slow chemical reactions take place [23]. Both the primary processes of exciton dynamics and charge separation occur in the presence of a protein (and solvent) environment at ambient temperature. In the framework of Förster's resonance excitation transfer theory [12], the energy transfer is so fast that both fluorescence and recombination (due to the environment) can be neglected.

When modeling these primary exciton transfer (ET) processes, the light-sensitive molecule is usually associated with a geometrically localized site, n, having excited electron energy E_n [23, 31]. The total number of sites, N, depends on the photosynthetic system. For example, $N = 15$ in the CP29 LHC which is closely associated with photosystem II (PSII) [24]. The sites interact via dipole-dipole (or exchange) interaction, which is described by matrix elements V_{nm}. Similar to many molecular systems, the simplest unit of this picture is a dimer, which describes the interaction between two (not necessarily neighboring) sites. The dimer is characterized by a donor (site n) and an acceptor (site m). Denote by $\Delta E_{nm} = E_n - E_m$ the difference between the two excited electron energy levels. The donor and acceptor can be weakly coupled ($|V_{nm}/\Delta E_{nm}| \ll 1$) or they can be strongly coupled ($|V_{nm}/\Delta E_{nm}| \gtrsim 1$) [3]. The dimer is embedded in, and interacting with, a protein-solvent environment. One then introduces the constants of interaction λ_n and λ_m characterizing the strength of the interaction between the dimer sites and the environment. The protein-solvent environment is characterized by its correlation function, which depends on the temperature and some parameters which describe the spectral density (the 'spectral function') of protein-solvent fluctuations at low and high frequencies. In order to describe different environmental effects, this correlation function can be taken to vary from a quite standard form [33] to a rather complicated one [27].

The quantum dynamics of the dimer is characterized by its 2×2 time-dependent reduced density matrix, which is obtained from the 'total' dimer-environment density matrix by averaging over (tracing out) the environmental degrees of freedom. The reduced dimer dynamics is then formally equivalent to that of an effective spin $1/2$. The protein-solvent environment is often modeled by a set of linear quantum oscillators (bosonic degrees of freedom) which characterize the dynamics of the protein and solvent atoms. In this "spin-boson" model, the interaction between the dimer and the environment is usually reduced to the self-consistent (adiabatic) renormalization of the dimer "donor" and "acceptor" energy levels [38, 18]. See also [6, 7, 30, 32, 34, 35] for different approaches. This so-called "diagonal interaction" [38] can be generalized, if needed, to a "non-diagonal interaction" [18].

The dynamics of the diagonal components of the reduced dimer density matrix (relative to the energy basis) is characterized by the ET rate. The dynamics of the non-diagonal components of the reduced density matrix is characterized by the decoherence rate. It describes the evolution of quantum coherent effects which are currently the focus of intense theoretical and experimental studies [23, 36] (see also references therein).

Even the relatively simple spin-boson model has surprisingly many unresolved and rather subtle theoretical issues. The first one is related to the structure of the dimer electron energy

spectrum. A real dimer based, for example, on two chlorophyll molecules, has many vibrational degrees of freedom [37, 9, 39, 1]. This means that the Hilbert space of the electron energy spectrum of a dimer is in actual fact very complicated (not two-dimensional!), with the two-level effective spin $1/2$ system only being a reasonable approximation to reality. The second issue is related to the protein-solvent environment. There are many models which describe this environment, but there is no consensus or clear understanding as to which one is the right one [23]. The third issue is related to the dimer-environment interaction. The problem is that the interaction constants λ_n and λ_m are not small (compared to V_{nm}). A standard perturbation theory can therefore not be used. Indeed, the famous Marcus formula for the electron transfer rate, γ, from an initially populated donor has the form, $\gamma \propto (1/\lambda) \exp(-f(\lambda)/\lambda^2)$ [38], where the interaction constant, λ, appears in the denominators of both the prefactor and in the exponent. In the standard perturbation theory approach (such as the Bloch-Redfield theory [18]), the rate is proportional to λ^2. It is therefore clear that the Marcus rate cannot be derived by using a standard perturbative approach.

In this paper, we resolve the third issue mentioned above, i.e., we develop a theory which allows for strong (indeed, arbitrary) values of the interactions. The donor and the acceptor of the dimer can be localized close to each other ($\lesssim 1nm$). For a protein-solvent environment whose correlation length exceeds this distance, it is reasonable to consider the donor and acceptor to be coupled to a single reservoir, a situation which we call the collective reservoir model. The opposite case, when each dimer site is coupled to its own, independent environment, is called the local reservoirs model. Collective and local interactions were discussed previously in [36] (see also references therein) and in [26] for stochastic environments. The advantage of the current work is that our mathematical analysis is rigorous, meaning that any approximation made can be controlled, and conditions of validity of these approximations can be given. This is especially important because, as mentioned above, standard perturbation approaches can not be used.

The main result of this work is a controlled expansion, for small V_{nm}, of the reduced dimer density matrix, valid for all times $t \geq 0$ and for arbitrary coupling constants λ_1, λ_2 and temperatures T. From this expansion, we derive the rates of the processes of electron (excitation) transfer and decoherence. We show that in certain regimes, those rates coincide with the expressions obtained previously from the usual Marcus formula.

We discuss the conditions on the spectral function of the reservoir at low frequencies which lead to long-time quantum coherences. This issue is of significant interest in recent research on the ET dynamics in LHCs, see e.g. [1] and references therein.

The paper is organized as follows. In Section 2, we describe the model and give an outline of our main results. In Section 3, we give the results in more mathematical detail and present the results of our numerical simulations. Section 4 is devoted to the mathematical approach of the dynamical resonance theory. We summarize our results in a Conclusion section. Finally, in Appendices A-E we present the detailed derivation of a few intermediate results.

2   Description of the model

We consider two types of dimer-reservoir interactions. In one, both dimer sites are coupled to the *same*, collective, heat bath. In the other one, each dimer site is coupled to an *independent*,
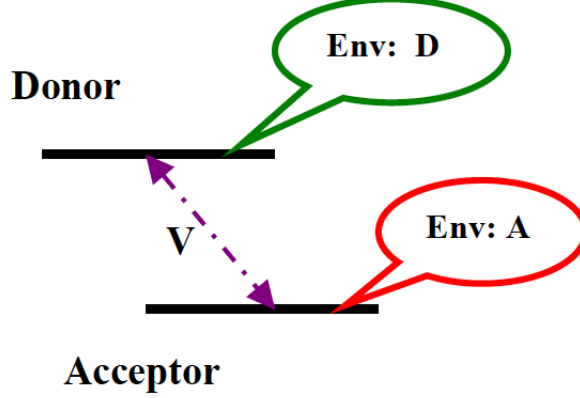
Figure 1: (Color online) The schematic of the chlorophyll dimer (D-donor, A-acceptor) interacting with the protein-solvent environments.

local, heat bath. The Hamiltonian of the **collective reservoir model** is

$$H_{\text{col}} = \frac{1}{2} \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix} + H_{\text{R}} + \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \otimes \phi(g), \tag{2.1}$$

where

$$H_{\text{R}} = \sum_k \omega_k a_k^\dagger a_k, \quad \text{and} \quad \phi(g) = \frac{1}{\sqrt{2}} \sum_k g_k a_k^\dagger + \text{h.c.} \tag{2.2}$$

Here, $\omega_k > 0$ is the frequency of mode k and $g_k \in \mathbb{C}$ is the 'form factor', determining how strongly the mode k is coupled to the dimer. While the quantities in (2.2) are written down for discrete modes indexed by k, we consider a reservoir with *continuous modes*, where k becomes a continuous variable (e.g. $k \in \mathbb{R}$ or a finite interval in $\mathbb{R}$, or $k \in \mathbb{R}^3$). Protein-solvent environments are usually described by an ensemble of atoms, called a "molecular reservoir model", in contrast to an ensemble of modes like phonons (see also [29]). In Sections 4 and E, we discuss the relation between these two environment models and we show that they both lead to the same results for the exciton transfer dynamics discussed in this paper.

In the continuous mode limit, the form factor g_k and the creation and annihilation operators $a_k^\dagger$, a_k become functions of the continuous variable k, which we denote by $g(k)$ and $a^*(k)$, $a(k)$, respectively.

The Hamiltonian of the **local reservoirs model** is

$$H_{\text{loc}} = \frac{1}{2} \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix} + H_{\text{R}_1} + H_{\text{R}_2} + \lambda_1 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \otimes \phi_1(g_1) + \lambda_2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \phi_2(g_2). \tag{2.3}$$

Now we have *two* form factors $g_1(k)$, $g_2(k)$ and *two* sets of creation and annihilation operators, $a_j^*(k)$ and $a_j(k)$, $j = 1, 2$. The values $j = 1, 2$ label the reservoirs. All operators of one reservoir commute with all those of the other.

We consider **initial states** of the form

$$\rho_{\text{in}} = \rho_{\text{S}} \otimes \rho_{\text{R}} \quad \text{or} \quad \rho_{\text{in}} = \rho_{\text{S}} \otimes \rho_{\text{R}_1} \otimes \rho_{\text{R}_2} \tag{2.4}$$

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for the collective or local models, respectively. Here, ρ_S is an arbitrary initial density matrix of the dimer and ρ_R, ρ_{R_1}, ρ_{R_2} are the reservoir equilibrium states at a temperature $T = 1/\beta > 0$. The **reduced dimer density matrix** at time t is obtained by evolving the whole dimer-reservoir density matrix and then tracing out the reservoirs,

$$\rho_S(t) = \text{Tr}_{\text{Reservoir(s)}}\left(e^{-itH}\rho_{\text{in}}e^{itH}\right). \tag{2.5}$$

Here, $H = H_{\text{col}}$ or $H = H_{\text{loc}}$, depending on the model considered.

The chlorophyll molecules in the dimer have the optical transitional frequencies, with excited energy levels $E_{\text{exc}} \approx 1.5 - 2.5\text{eV}$. The thermal bath usually has much lower excited modes energy, $E_T \approx 25\text{meV}$.

2.1 Outline of results

Our main goal is to describe the dynamics of the reduced dimer density matrix. In Theorems 3.1 and 3.3 below, we give the law of evolution of the populations (diagonal elements of the density matrix in the energy basis) and of decoherence (off-diagonal). These results exhibit a main term in the dynamics and a remainder which is *controlled for all times* $t \geq 0$. In order to derive the dynamical laws mathematically, we need to impose a regularity condition on the form factors g, $g_{1,2}$ in (2.1), (2.3). It is best expressed as a condition on the **spectral function of the reservoir**, which is defined as [18, 15]

$$J(\omega) = \sqrt{2\pi}\,\tanh(\beta\omega/2)\,\widehat{\mathcal{C}}(\omega), \qquad \omega \geq 0, \tag{2.6}$$

where $\widehat{\mathcal{C}}(v) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-ivt}\mathcal{C}(t)\mathrm{d}t$, $v \in \mathbb{R}$, is the Fourier transform of the symmetrized correlation function

$$\mathcal{C}(t) = \tfrac{1}{2}\left(\langle\phi_t(g)\phi(g)\rangle_\beta + \langle\phi(g)\phi_t(g)\rangle_\beta\right). \tag{2.7}$$

Here, $\langle\cdot\rangle_\beta$ is the average of a reservoir observable in the reservoir equilibrium at temperature $T = 1/\beta$, g is the form factor appearing in (2.1), (2.3) and $\phi_t(g) = e^{itH_R}\phi(g)e^{-itH_R}$, H_R the uncoupled Hamiltonian of the reservoir(s). Of course, in the model where we have two reservoirs, there are two corresponding spectral functions $J_1(\omega)$, $J_2(\omega)$. We point out that the product $\tanh(\beta\omega/2)\widehat{\mathcal{C}}(\omega)$ appearing in the definition (2.6) is actually *independent* of β, expressible purely in terms of the form factor (c.f. [18, 15] and also Section E). The mathematical regularity condition we impose (for each reservoir) is

$$J(\omega) = \frac{\omega^{2p+2}}{(1+\omega)^\sigma}\widetilde{J}(\omega), \tag{2.8}$$

where

$$p = \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \tfrac{7}{2}, \quad \text{or} \quad p > 4 \quad \text{and} \quad \sigma > 3/2, \tag{2.9}$$

and where $\widetilde{J}(\omega)$ is a bounded function of $\omega \geq 0$. We remark that in principle, a 'minimal condition' on the low-modes behavior is $p > -1/2$, but so far our mathematical techniques require the more restrictive values in (2.9).[1]

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[1]While our current rigorous mathematical approach requires the restriction (2.9) on p, we believe that the only 'rigid' requirement is $p > -1/2$. This same restriction occurs in Leggett's work [15] and is needed

2.1.1 Relaxation of the dimer

We denote the population of site (level) 1 by

$$p(t) = \langle \varphi_1, \rho_S(t)\varphi_1 \rangle = [\rho_S(t)]_{11}, \tag{2.10}$$

where the dimer site basis for $V = 0$ (or, energy basis) is

$$\varphi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \varphi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.11}$$

The initial population is $p(0) \in [0,1]$. We show in Theorem 3.1 that, for arbitrary values of λ_1 and λ_2 and sufficiently small values of V, and for *all times* $t \geq 0$,

$$p(t) = p_\infty + e^{-\gamma t}(p(0) - p_\infty) + R(t). \tag{2.12}$$

The relation (2.12) is valid for both the local and collective reservoirs models, with different expressions for the relaxation rate γ. Namely, γ takes specific values γ_{col} and γ_{loc} (c.f. (2.25)) for the collective and local reservoirs models, which we discuss below in Section 2.1.3. It satisfies $\gamma \propto V^2$ and $\gamma > 0$ for $V > 0$. The remainder term has the bound $|R(t)| \leq C/t$ for some constant C. The final value p_∞ is the population of the dimer at equilibrium with the reservoir(s),

$$p_\infty = \frac{e^{-\frac{\beta}{2}(\epsilon - \alpha_1)}}{e^{-\frac{\beta}{2}(\epsilon - \alpha_1)} + e^{-\frac{\beta}{2}(-\epsilon - \alpha_2)}} + O(V) = \frac{1}{1 + e^{\beta\hat\epsilon}} + O(V), \tag{2.13}$$

where

$$\hat\epsilon = \hat\epsilon(\lambda_1, \lambda_2) = \epsilon - \frac{\alpha_1 - \alpha_2}{2}. \tag{2.14}$$

Here, $\alpha_{1,2} \geq 0$ are *renormalizations* of the dimer donor and acceptor energies (see Section 3.1), which are caused by the interaction with the reservoir(s). Their precise expressions are given in (3.1) and they satisfy $\alpha_j \propto \lambda_j^2$.

Discussion

- *Properties of the final population p_∞.*

  If $\alpha_1 = \alpha_2$ then we say that the reservoirs are *coupled in a symmetric way* to the dimer, and we have $\hat\epsilon = \epsilon > 0$. This happens for instance if $\lambda_1^2 = \lambda_2^2$ and, for the local reservoirs case, if additionally $g_1 = g_2$.

  However, the sign of $\hat\epsilon$ can be positive or negative depending on which reservoir coupling constant is stronger. From (2.14) and $\alpha_j \propto \lambda_j^2$ we see readily that if $\lambda_1^2 \gg \max\{\lambda_2^2, \epsilon\}$ then $\hat\epsilon \propto -\lambda_1^2$ and if $\lambda_2^2 \gg \max\{\lambda_1^2, \epsilon\}$ then $\hat\epsilon \propto \lambda_2^2$. For high temperatures we have

$$p_\infty \approx \frac{1}{2} - \frac{\hat\epsilon}{T}, \qquad T \gg |\hat\epsilon|. \tag{2.15}$$

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in the application of a unitary transformation (polaron transformation, which is defined only if $p > -1/2$) to obtain a Hamiltonian in which $\lambda_{1,2}$ do not have to be considered to be small parameters, but where V is the small perturbation parameter. An improvement of our current mathematical approach is likely to remove some of the restriction on p. See Sections C and E for further detail on this point.

The small correction to the value $1/2$ is *negative* for the symmetrically coupled case ($\hat{\epsilon} = \epsilon$) and if level two is coupled to the reservoir(s) much more strongly than level one. If the level one is coupled more strongly, then that correction is *positive*. This shows that if one level is coupled more strongly to the reservoir(s) than the other, the final population of the more strongly coupled level is increased. While this effect is small for high temperatures (see (2.15)), it is large for low temperatures:

$$p_\infty \approx \begin{cases} 1, & \text{if } \lambda_1^2 \gg \max\{\lambda_2^2, \epsilon\} \\ 0, & \text{if } \lambda_2^2 \gg \lambda_1^2 \end{cases} \quad \text{and} \quad T \ll |\hat{\epsilon}| \tag{2.16}$$

We conclude that if $T \ll |\hat{\epsilon}|$, then one can entirely populate level one by coupling it very strongly to the reservoir(s), or entirely depopulate it by coupling the other level very strongly to the reservoir(s).

- *Domain of usefulness of expansion* (2.12).

  The expansion is meaningful if

$$|R(t)| \leq |p_\infty + \mathrm{e}^{-\gamma t}(p(0) - p_\infty)|. \tag{2.17}$$

  If $\gamma t \ll 1$ then the right side is just $p(0)$ and so the bound is satisfied if in addition $t \geq C/p(0)$, where C is the constant in the upper bound of $R(t)$ (see before (2.13)). Hence (2.17) holds for

$$C/p(0) \ll t \ll 1/\gamma \propto V^{-2}. \tag{2.18}$$

  This is useful if $p(0)$ is not very small. Other domains can be found as follows. If $p(0) - p_\infty \geq 0$ then (2.17) is satisfied for $t \geq C/p_\infty$. Similarly, if $p(0) - p_\infty < 0$, then we have $q(0) - q_\infty > 0$, where $q(t) = 1 - p(t)$ and $q_\infty = 1 - p_\infty$ are the level 2 populations. Now (2.12) gives $q(t) = q_\infty + \mathrm{e}^{-\gamma t}(q(0) - q_\infty) - R(t)$, where the remainder is the same as in (2.12). Hence, this remainder is small compared to the main term for $t \geq C/q_\infty$. At high temperatures, $p_\infty \approx 1/2 \approx q_\infty$ and the remainder is small for times $t \geq 2C$, regardless of the initial condition.

- *A different remainder estimate.* The dynamical resonance theory of [13] which we use to prove the expansion (2.12) is designed to give a remainder that decays as $t \to \infty$. Instead, one can modify this theory to yield a remainder which is $O(V)$ for all times, but may not vanish at $t = \infty$.

2.1.2 Decoherence of the dimer

Let

$$[\rho_\mathrm{S}(t)]_{12} = \langle \varphi_1, \rho_\mathrm{S}(t)\varphi_2 \rangle$$

be the off-diagonal density matrix of the dimer in the basis (2.11). We show in Theorem 3.3 that for arbitrary λ_1, λ_2, for small enough V, and *all times $t \geq 0$,*

$$[\rho_\mathrm{S}(t)]_{12} = \mathrm{e}^{-\gamma t/2}\, \mathrm{e}^{-it(\hat{\epsilon} + x_\mathrm{LS})}\, \mathrm{e}^{-\Gamma_\infty}\, [\rho_\mathrm{S}(0)]_{12} + O(V) + R(t), \tag{2.19}$$

where γ is the relaxation rate (the same as in (2.12), see (2.25) for the explicit expression) and $x_\mathrm{LS} \in \mathbb{R}$ is the Lamb shift (c.f. (3.14)). Relation (2.19) is valid for both the local and collective

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reservoirs models (the γ having different expressions). The term $O(V)$ is independent of time t, and $R(t)$ satisfies $|R(t)| \leq C/t$, for some constant C. The constant $\Gamma_\infty \geq 0$ is given explicitly in (3.12). It describes the large time decoherence of the dimer under the dynamics with $V = 0$. Namely, for $V = 0$ the dimer dynamics can be solved exactly (see Section B.2),

$$[\rho_S(t)]_{12} = e^{-it\hat{e}} \mathcal{D}(t) [\rho_S(0)]_{12}, \qquad (V = 0) \tag{2.20}$$

where $\mathcal{D}(t)$ (which can be expressed in terms of a reservoir correlation function, see Section B.4) satisfies

$$\lim_{t\to\infty} \mathcal{D}(t) = e^{-\Gamma_\infty}. \tag{2.21}$$

Discussion

- *Two regimes: full and partial phase decoherence* $(V = 0)$

  The dynamics for $V = 0$ leaves the populations invariant, and the off-diagonal density matrix element of the dimer (energy basis) satisfies

  $$\left|[\rho_S(t)]_{12}\right| = \left|[\rho_S(0)]_{12}\right| \begin{cases} e^{-\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 Q_2(t)} & \text{collective reservoir} \\ e^{-\frac{1}{\pi}\lambda_1^2 Q_2^{(1)}(t)} e^{-\frac{1}{\pi}\lambda_2^2 Q_2^{(2)}(t)} & \text{local reservoirs} \end{cases} \quad (V = 0), \tag{2.22}$$

  for some functions $Q_2(t), Q_2^{(j)}(t) \geq 0$ (see (2.26), (2.27)). The process described by (2.22) is called phase decoherence. We say that *full* phase decoherence takes place if $[\rho_S(t)]_{12} \to 0$ as $t \to \infty$. Otherwise we call the phase decoherence *partial*. Full phase decoherence happens if and only if $\lim_{t\to\infty} Q_2(t) = \infty$ and $\lambda_1 \neq \lambda_2$ (collective) or at least one $\lim_{t\to\infty} Q_2^{(j)}(t) = \infty$ and $\lambda_j \neq 0$ (local). We show in (3.13) that

  $$\text{Full phase decoherence} \qquad \Longleftrightarrow \qquad p \leq 0, \tag{2.23}$$

  where p is the parameter in (2.8) (see also Section B.4).

  In the situation of partial phase decoherence (for $V = 0$), i.e., when $p > 0$, the spectral function of the reservoir, (2.8), satisfies $J(\omega) \to 0$ as $\omega \to 0$. This low-mode behavior of J is not always satisfied in noisy protein environments. In particular, it is not true in the presence of the so-called $1/f$ noise [8]. At the same time, a vanishing spectral density in the limit of low frequencies can be realized in many LHCs, see [1] (as well references therein).

  Our technical condition (2.9), used to derive the evolution of the dimer mathematically rigorously, places us in the regime of partial phase decoherence. But as mentioned above, we expect that the mathematical analysis can be pushed to cover the range $p > -1/2$. It is then reasonable to include a discussion of the relaxation rates in the situation of full phase decoherence $(-1/2 < p \leq 0)$ as well, in what follows.

- *Domain of usefulness of expansion* (2.19).

  Analogously to the discussion of (2.17), one sees that the remainder in (2.19) is small if

  $$Ce^{\Gamma_\infty}/[\rho_S(0)]_{12} \ll t \ll 1/\gamma \propto V^{-2}.$$

We may view $e^{-\Gamma_\infty}[\rho_S(0)]_{12}$ in (2.19) as a *shifted initial condition*, whose absolute value (but not phase) is that of the asymptotic dynamics with $V = 0$. Under the dynamics with $V = 0$, the absolute value of the off-diagonal matrix element reaches its final value $e^{-\Gamma_\infty}|[\rho_S(0)]_{12}|$ at the reservoir correlation time independent of V (c.f. (2.21), (B.6), Lemma 2.1). For V small, the factor $e^{-\gamma t/2} \approx 1$ in (2.19) has not yet started to decay at that point in time.

- *Possible improvement of the resonance expansion for small times.*

  We expect that an expansion (2.19) holds with $e^{-\Gamma_\infty}$ replaced by 1 and a remainder $R(t) = O(V)$ for all times. However, the existing dynamical resonance theory must be modified to reach that result. In its present form, it is not accurate to describe decoherence for small times. Indeed, it follows from (2.19) that $R(0) = [\rho_S(0)]_{12} \cdot O(1 - e^{-\Gamma_\infty}) + O(V)$, which may not be small. We explain how the factor $e^{-\Gamma_\infty}$ appears naturally within the resonance description of the dynamics, and why it is not present (rather, $\Gamma_\infty = 0$) in the dynamics of the populations. See Section B.3, equation (B.18).

- *Relation between decoherence and relaxation rates for arbitrary interaction strength.*

  It is well known from the Bloch-Redfield weak coupling theory that if λ is small and $J(0) = 0$, then the relaxation rate γ_{relax} (decay of diagonal) and the decoherence rate γ_{deco} (decay of off-diagonal) satisfy the relation

$$\gamma_{\text{deco}} = \gamma_{\text{relax}}/2. \tag{2.24}$$

  Our results (2.12) and (2.19) show that the relation (2.24) is *valid for arbitrary λ*.

2.1.3 Relaxation rates

The relaxation rates of the collective and local reservoirs models are given by

$$\gamma_{\text{col}} = V^2 \lim_{r \to 0_+} \int_0^\infty e^{-rt} \cos(\hat{\epsilon}t) \, \cos\left[\frac{(\lambda_1 - \lambda_2)^2}{\pi}Q_1(t)\right] \exp\left[-\frac{(\lambda_1 - \lambda_2)^2}{\pi}Q_2(t)\right] dt,$$
$$\gamma_{\text{loc}} = V^2 \lim_{r \to 0_+} \int_0^\infty e^{-rt} \cos(\hat{\epsilon}t) \, \cos\left[\frac{\lambda_1^2}{\pi}Q_1^{(1)}(t) + \frac{\lambda_2^2}{\pi}Q_1^{(2)}(t)\right] \exp\left[-\frac{\lambda_1^2}{\pi}Q_2^{(1)}(t) - \frac{\lambda_2^2}{\pi}Q_2^{(2)}(t)\right] dt, \tag{2.25}$$

where $\hat{\epsilon}$ is defined in (2.14) and where (collective reservoir)

$$Q_1(t) = \int_0^\infty \frac{J(\omega)}{\omega^2} \sin(\omega t) d\omega,$$
$$Q_2(t) = \int_0^\infty \frac{J(\omega)(1 - \cos(\omega t))}{\omega^2} \coth(\beta\omega/2) d\omega \tag{2.26}$$

and (local reservoirs)

$$Q_1^{(j)}(t) = \int_0^\infty \frac{J_j(\omega)}{\omega^2} \sin(\omega t) d\omega,$$
$$Q_2^{(j)}(t) = \int_0^\infty \frac{J_j(\omega)(1 - \cos(\omega t))}{\omega^2} \coth(\beta\omega/2) d\omega. \tag{2.27}$$

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The limit $r \to 0_+$ appears in (2.25) because the analysis involves Green's functions close to the real axis. The correctness of the formula (2.25) depends crucially on the presence of this limit when the function to be integrated does not decay to zero as $t \to \infty$. This happens in the case of partial phase decoherence, where $Q_2(t) \not\to \infty$ for large times. In the contrary case, when the integrand in (2.25) for $r = 0$ is integrable, we can leave out the limit in the expression for γ_{col} and γ_{loc} (just set $r = 0$). Both situations are reasonable, but they need to be discussed separately. Note that for $\lambda_1 = \lambda_2$, we obtain from (2.25) that $\gamma_{\mathrm{col}} = 0$ (for $\epsilon \neq 0$).

Remark. The expansion (2.12) is valid for small values of V. In particular (see (D.3)), $V \leq \mathrm{const.}\widetilde{\gamma}$, where $\widetilde{\gamma}$ is $\gamma_{\mathrm{col}}/V^2$ or $\gamma_{\mathrm{loc}}/V^2$ (which is independent of V). One can expand γ, (2.25), for small λ. To lowest order (λ^2), one then recovers the expression predicted by the Bloch-Redfield theory (Fermi golden rule) in the weak coupling limit (small λ). This has been shown in [18], Section 5.

We now give more manageable expressions of $\gamma_{\mathrm{col}}, \gamma_{\mathrm{loc}}$ than (2.25), in both regimes of full and of partial phase decoherence. These easier (approximate) expressions are given in (2.31), (2.33) and (2.35), (2.41) and are derived from (2.25) in Section 2.1.4. Let us consider spectral functions of the reservoir of the form (2.9) with $p > -1/2$ and with an exponential high-mode cutoff $\omega_c > 0$,

$$J(\omega) = A_p\, \omega^{2p+2}\mathrm{e}^{-\omega/\omega_c}, \tag{2.28}$$

where $A_p > 0$. In the local reservoirs model, each reservoir's spectral function $J_j(\omega)$ is of the form (2.28) with possibly different p and ω_c. Set

$$\nu = \int_0^\infty \frac{J(\omega)}{\omega}\mathrm{d}\omega = A_p\, \omega_c^{2p+2}\int_0^\infty y^{2p+1}\mathrm{e}^{-y}\mathrm{d}y \qquad \text{and} \qquad \nu_j = \int_0^\infty \frac{J_j(\omega)}{\omega}\mathrm{d}\omega. \tag{2.29}$$

Dimensionalities. We adopt units in which $\hbar = 1$. The dimensions are as follows.
  – Dimensionless quantities: $J(\omega)$, ν, ν_j, $A_p\omega^{2p+2}$
  – Dimension energy: ϵ, ω, ω_c, T, λ_j^2
  – Dimension 1/energy: Q_j, $Q_j^{(k)}$, $g_j(k)$ (c.f. (2.3))

Since the spectral function (2.28) is dimensionless, the coefficient A_p has the same dimension as ω^{-2p-2}, which is (energy)$^{-2p-2}$ and depends on p. $J(\omega)$ is quadratic in the form factor(s) g (g_j) (c.f. (2.6), (2.7)) and the form factor(s) are defined only up to multiplication with the coupling constants λ_1, λ_2, see (2.1) and (2.3). Therefore, only the combination $\lambda_j\sqrt{A_p}$ ever appears. The expressions for the relaxation rates do not depend on A_p.

Relaxation rate in the regime of partial phase decoherence, $p > 0$.
Consider first the **collective reservoir** model and the regime

$$\omega_c \ll T, \quad (\lambda_1 - \lambda_2)^2\nu \ll \omega_c^2/T \quad \text{and} \quad |\epsilon - \tfrac{\nu}{\pi}(\lambda_1^2 - \lambda_2^2)| \ll \omega_c. \tag{2.30}$$

The first inequality in (2.30), $\beta\omega_c \ll 1$, is called the high temperature regime [38] and usually covers room temperatures. The dimer relaxation rate (2.25) has the (approximate) expression

$$\gamma_{\mathrm{col}} = V^2\omega_c^{-1}\big(1 - \mathrm{e}^{-\frac{2TB}{\pi}(\lambda_1 - \lambda_2)^2}\big), \tag{2.31}$$

where $B = B(p, \omega_c) = \int_0^\infty \frac{J(\omega)}{\omega^3}\mathrm{d}\omega$. For instance, $B(1/2, \omega_c) = A_{1/2}\,\omega_c$.

Similarly, for the **local reservoirs** model, the spectral functions of the reservoirs are given by (2.28) with (possibly different) $p_j > 0$ and $\omega_{j,c}$. For ease of notation, we take $\omega_{1,c} \approx \omega_{2,c} \approx \omega_c$ and $p_1 \approx p_2 \approx p$ (the following bounds can be easily derived also when this approximate symmetry does not hold). In the high-temperature regime

$$\omega_c \ll T, \qquad \lambda_j^2 \nu_j \ll \omega_c^2/T, \ j = 1, 2 \qquad \text{and} \qquad |\epsilon - \tfrac{1}{\pi}(\nu_1 \lambda_1^2 - \nu_2 \lambda_2^2)| \ll \omega_c, \qquad (2.32)$$

the relaxation rate (2.25) is given by

$$\gamma_{\mathrm{loc}} = V^2 \omega_c^{-1} \big(1 - \mathrm{e}^{-\frac{2T}{\pi}(B_1 \lambda_1^2 + B_2 \lambda_2^2)}\big), \qquad (2.33)$$

where $B_j = B_j(p_j, \omega_{j,c}) = \int_0^\infty \frac{J_j(\omega)}{\omega^3} \mathrm{d}\omega$.

Dimer relaxation in the regime of full phase decoherence, $-1/2 < p \leq 0$.
Consider first the **collective reservoir** model in the parameter region

$$\omega_c \ll T \quad \text{and} \quad \omega_c^2 \ll (\lambda_1 - \lambda_2)^2 T \nu, \qquad (2.34)$$

which also corresponds to the high-temperature regime. The dimer relaxation rate (2.25) has the (approximate) expression

$$\gamma_{\mathrm{col}} = \left(\frac{V}{2}\right)^2 \sqrt{\frac{2\pi}{T(\epsilon_{\mathrm{col},1} + \epsilon_{\mathrm{col},2})}} \left\{ \exp\left[-\frac{(\epsilon - \epsilon_{\mathrm{col},1})^2}{2T(\epsilon_{\mathrm{col},1} + \epsilon_{\mathrm{col},2})} \right] + \exp\left[-\frac{(\epsilon + \epsilon_{\mathrm{col},2})^2}{2T(\epsilon_{\mathrm{col},1} + \epsilon_{\mathrm{col},2})} \right] \right\} \qquad (2.35)$$

where two *reconstruction energies* are introduced,

$$\epsilon_{\mathrm{col},j} = 2\frac{\nu}{\pi}(\lambda_j^2 - \lambda_1 \lambda_2), \qquad j = 1, 2. \qquad (2.36)$$

We call (2.35) the **Generalized Marcus Formula** (see the discussion after (2.39)). As $\epsilon_{\mathrm{col},1} + \epsilon_{\mathrm{col},2} = 2\frac{\nu}{\pi}(\lambda_1 - \lambda_2)^2$, the second condition in (2.34) is equivalent to

$$\omega_c^2 \ll T(\epsilon_{\mathrm{col},1} + \epsilon_{\mathrm{col},2}). \qquad (2.37)$$

For symmetric coupling, $\lambda_1 = -\lambda_2 = \lambda$, we have $\epsilon_{\mathrm{col},j} = \epsilon_{\mathrm{col}} = 4\nu\lambda^2/\pi$ (for $j = 1, 2$) and (2.36) takes the form

$$\gamma_{\mathrm{col}} = \left(\frac{V}{2}\right)^2 \sqrt{\frac{\pi}{T\epsilon_{\mathrm{col}}}} \Big(\mathrm{e}^{-\frac{(\epsilon - \epsilon_{\mathrm{col}})^2}{4T\epsilon_{\mathrm{col}}}} + \mathrm{e}^{-\frac{(\epsilon + \epsilon_{\mathrm{col}})^2}{4T\epsilon_{\mathrm{col}}}}\Big), \qquad (2.38)$$

which coincides with the heuristically derived rate given in [38]. Typically, the second exponential is much smaller than the first one ($\epsilon, \epsilon_{\mathrm{col}} > 0$) and is therefore neglected. The resulting formula,

$$\gamma_{\mathrm{col}} = \left(\frac{V}{2}\right)^2 \sqrt{\frac{\pi}{T\epsilon_{\mathrm{col}}}} \mathrm{e}^{-\frac{(\epsilon - \epsilon_{\mathrm{col}})^2}{4T\epsilon_{\mathrm{col}}}}, \qquad (2.39)$$

is the famous **Marcus Formula** of electron transfer [16, 17]. Hence the name Generalized Marcus Formula for (2.35), which extends the original one to the situation where the donor and acceptor may be coupled in an asymmetric way to a common reservoir. The energies $\epsilon_{\mathrm{col},j}$, (2.36), play the role of generalized reorganization (reconstruction) energies.

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Similarly, for the **local reservoirs** model, in the high-temperature regime

$$\omega_{j,c} \ll T \quad \text{and} \quad \omega_{j,c}^2 \ll \lambda_j^2 T \nu_j, \quad j = 1, 2, \tag{2.40}$$

the dimer relaxation rate (2.25) has the expression,

$$\gamma_{\text{loc}} = \left(\frac{V}{2}\right)^2 \sqrt{\frac{2\pi}{T(\epsilon_{\text{loc},1} + \epsilon_{\text{loc},2})}} \left\{ \exp\left[-\frac{(\epsilon - \epsilon_{\text{loc},1})^2}{2T(\epsilon_{\text{loc},1} + \epsilon_{\text{loc},2})}\right] + \exp\left[-\frac{(\epsilon + \epsilon_{\text{loc},2})^2}{2T(\epsilon_{\text{loc},1} + \epsilon_{\text{loc},2})}\right] \right\}, \tag{2.41}$$

where the generalized reorganization (reconstruction) energies are

$$\epsilon_{\text{loc},j} = 2\frac{\nu_j}{\pi}\lambda_j^2, \qquad j = 1, 2. \tag{2.42}$$

Discussion

- For $\lambda_1 = -\lambda_2$, γ_{col} (2.35) reduces to the form derived in [38]. If in addition $\nu_1 = \nu_2$, then $\gamma_{\text{col}} = \gamma_{\text{loc}}$. The rate γ_{loc} is a symmetric function of the coupling constants λ_1 and λ_2 (each reservoir acts independently in the same way), but γ_{col} is not. Indeed, γ_{loc} only depends on the absolute values of the λ_j, while γ_{col} depends also on the sign of the product $\lambda_1\lambda_2$. If $\lambda_1 = 0$ or $\lambda_2 = 0$, then $\gamma_{\text{col}} = \gamma_{\text{loc}}$.

- The *reconstruction energies* $\epsilon_{\text{col},j}$ of the collective reservoir model can be positive or negative, depending on the relative values and signs of the coupling constants. However, in the local reservoirs model, $\epsilon_{\text{loc},j} \geq 0$ always.

- *Upper bound on γ_{col} in the high-temperature regime.* According to (2.35) and (2.37) we have

$$\gamma_{\text{col}} < 2\sqrt{2\pi}(V/2)^2/\omega_c. \tag{2.43}$$

2.1.4 Derivation of (2.31), (2.33) and (2.35), (2.41) from (2.25)

Derivation of (2.31). The process is governed by two parameters: the (finite) asymptotic value

$$\lim_{t \to \infty} Q_2(t) \equiv Q_2(\infty) = \int_0^\infty \frac{J(\omega)}{\omega^2} \coth(\beta\omega/2)\mathrm{d}\omega \tag{2.44}$$

and the characteristic time

$$t_* = 1/\omega_c \qquad \text{provided } \beta\omega_c \ll 1 \tag{2.45}$$

at which $Q_2(t)$ approaches the value $Q_2(\infty)$.[2] To analyze γ_{col}, (2.25), we split the integration in two domains. For $t > t_*$, we replace $\mathrm{e}^{-\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 Q_2(t)} \approx \mathrm{e}^{-\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 Q_2(\infty)}$. From[3] $Q_1(t) \leq$

---

[2]To find the convergence speed of the limit (2.44), we calculate

$$\int_0^\infty \frac{J(\omega)\cos(\omega t)}{\omega^2}\coth(\beta\omega/2)\mathrm{d}\omega \propto \frac{T\omega_c}{(\omega_c t)^2 + 1} \qquad \text{for } \beta\omega_c \ll 1. \tag{2.46}$$

Here, we have used $p = 1/2$ (other values $p > 0$ give the same conclusion) and that, due to the high frequency cutoff ω_c in J (see (2.28)), the integration is essentially over $\omega \leq \omega_c$, and therefore $\coth(\beta\omega/2) \approx 2/\beta\omega$ provided $\beta\omega_c \ll 1$.

[3]We have $Q_1(t) = A_p \int_0^\infty \omega^{2p}\mathrm{e}^{-\omega/\omega_c}\sin(\omega t)\mathrm{d}\omega$ and upon making a change of variables $\omega' = \omega/\omega_c$, one immediately finds $Q_1(t) \leq CA_p\omega_c^{2p+1}$, where C is a dimensionless constant (depending on p).

$CA_p\omega_c^{2p+1}$ it follows that $\cos[\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 Q_1(t)] \approx 1$ if $(\lambda_1 - \lambda_2)^2 A_p \omega_c^{2p+1} \ll 1$. The last inequality is satisfied for (see (2.29))

$$(\lambda_1 - \lambda_2)^2 \nu \ll \omega_c. \tag{2.47}$$

Thus, under the conditions (2.45) and (2.47), the contribution to γ_{col} from the integration over $t \geq t_*$ is

$$V^2 e^{-\frac{1}{\pi}(\lambda_1-\lambda_2)^2 Q_2(\infty)} \lim_{r \to 0_+} \int_{t_*}^{\infty} e^{-rt} \cos(\hat\epsilon t) \mathrm{d}t = -V^2 e^{-\frac{1}{\pi}(\lambda_1-\lambda_2)^2 Q_2(\infty)} \frac{\sin(\hat\epsilon t_*)}{\hat\epsilon}$$

$$\approx -V^2 t_* e^{-\frac{1}{\pi}(\lambda_1-\lambda_2)^2 Q_2(\infty)}, \tag{2.48}$$

where we use in the last step $|\hat\epsilon t_*| \ll 1$, or

$$|\hat\epsilon| \ll \omega_c. \tag{2.49}$$

Now we estimate the contribution to (2.25) for small times $t \leq t_*$. In this integral, we can set $r = 0$ to begin with and we expand the integrand in (2.25) as (t small)

$$\left(1 - \tfrac{1}{2}\hat\epsilon^2 t^2\right) \left[1 - \frac{(\lambda_1-\lambda_2)^4}{\pi^2}\nu^2 t^2\right] \left[1 - \frac{(\lambda_1-\lambda_2)^2}{\pi}T\nu t^2\right]$$

$$\approx 1 - t^2 \left(\hat\epsilon^2/2 + (\lambda_1-\lambda_2)^4 \nu^2/\pi^2 + (\lambda_1-\lambda_2)^2 T\nu/\pi\right). \tag{2.50}$$

The integral $\int_0^{t_*} ... \mathrm{d}t$ of (2.50) is then $t_* - \frac{t_*^3}{3}(\cdots)$ which we approximate by t_* under the condition that $\frac{t_*^3}{3}(\cdots) \ll t_*$, i.e., that $\hat\epsilon^2 + (\lambda_1-\lambda_2)^4 \nu^2 + (\lambda_1-\lambda_2)^2 T\nu \ll t_*^{-2} = \omega_c^2$. The latter inequality is implied by (2.30). Combining this with (2.48) and (2.45) gives

$$\gamma_{\text{col}} = V^2 \omega_c^{-1}\left(1 - e^{-\frac{1}{\pi}(\lambda_1-\lambda_2)^2 Q_2(\infty)}\right). \tag{2.51}$$

Further, again for $\beta\omega_c \ll 1$, we can replace $\coth(\beta\omega/2)$ in (2.44) by $2/\beta\omega$. Then $Q_2(\infty) \approx 2T \int_0^{\infty} \frac{J(\omega)}{\omega^3} \mathrm{d}\omega$ and so (2.31) follows from (2.51). Equation (2.33) is derived in the same way.

Derivation of (2.35). For $-1/2 < p \leq 0$ we have $Q_2(t) \to \infty$. The region of integration in (2.26) is essentially $\omega \leq \omega_c$, due to the high energy mode cutoff (2.28). Therefore, for $\beta\omega_c \ll 1$, we replace $\coth(\beta\omega/2) \approx 2/(\beta\omega)$ in (2.26), so that

$$Q_2(t) \approx 2T \int_0^{\infty} \frac{J(\omega)(1 - \cos(\omega t))}{\omega^3} \mathrm{d}\omega \approx T\nu t^2, \tag{2.52}$$

where the last approximation is valid for times t satisfying $\omega_c t \ll 1$ (in order that $1 - \cos(\omega t) \approx \frac{1}{2}\omega^2 t^2$). The approximation $Q_2(t) \approx T\nu t^2$ has also been used in [38]. As Q_2 is increasing, the exponential factor in (2.25) for $t \geq \omega_c^{-1}$ is estimated as

$$e^{-\frac{(\lambda_1-\lambda_2)^2}{\pi}Q_2(t)} \approx e^{-\frac{(\lambda_1-\lambda_2)^2}{\pi}T\nu t^2} \lesssim e^{-\frac{(\lambda_1-\lambda_2)^2}{\pi}T\nu/\omega_c^2} \ll 1,$$

provided

$$(\lambda_1 - \lambda_2)^2 T\nu \gg \omega_c^2. \tag{2.53}$$

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The region $t \geq \omega_c^{-1}$ can thus be neglected in the integral and (2.25) and we can also approximate $Q_1(t)$ in (2.26) by its behaviour for small times (see also [38]),

$$Q_1(t) \approx \nu t. \tag{2.54}$$

Consequently,

$$\gamma_{\mathrm{col}} = V^2 \int_0^\infty \cos(\hat\epsilon t) \cos[(\lambda_1 - \lambda_2)^2 \nu t/\pi] \, \mathrm{e}^{-\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 T \nu t^2} \, \mathrm{d}t. \tag{2.55}$$

Using $\cos(x)\cos(y) = \frac{1}{2}\{\cos(x+y) + \cos(x-y)\}$ and $\int_0^\infty \cos(bx)\mathrm{e}^{-ax^2}\mathrm{d}x = \sqrt{\pi/4a} \, \mathrm{e}^{-b^2/4a}$, we evaluate (2.55) explicitly to obtain (2.35). Relation (2.41) is obtained in the same way.

3 Main results: details

3.1 Energy renormalization

For the collective reservoir model and the local reservoirs model, repectively, set

$$\alpha_j = \frac{2\lambda_j^2 \nu}{\pi}, \quad j = 1,2 \qquad \text{and} \qquad \alpha_j = \frac{2\lambda_j^2 \nu_j}{\pi}, \quad j = 1,2, \tag{3.1}$$

where the ν, ν_j are given in (2.29). Consider H_{col}, (2.1) and H_{loc}, (2.3) with $V = 0$ and λ_1, λ_2 arbitrary. We show in Appendix B.1 that the equilibrium state of the interacting dimer-reservoir system at temperature $T = 1/\beta > 0$ for the model with the collective reservoir is

$$
\begin{aligned}
\rho_{\beta,\vec\lambda,0} &= \frac{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)}}{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)} + \mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}} \, |\varphi_1\rangle\langle\varphi_1| \otimes W^*\big(\lambda_1 g/(\mathrm{i}\omega)\big)\rho_{\mathrm{R}} W\big(\lambda_1 g/(\mathrm{i}\omega)\big) \\
&\quad + \frac{\mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}}{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)} + \mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}} \, |\varphi_2\rangle\langle\varphi_2| \otimes W^*\big(\lambda_2 g/(\mathrm{i}\omega)\big)\rho_{\mathrm{R}} W\big(\lambda_2 g/(\mathrm{i}\omega)\big),
\end{aligned} \tag{3.2}
$$

where

$$W(h) = \mathrm{e}^{\mathrm{i}\phi(h)} \tag{3.3}$$

is the unitary Weyl operator. By tracing out the reservoir in (3.2) we find

$$\mathrm{Tr}_{\mathrm{R}} \, \rho_{\beta,\vec\lambda,0} = \frac{\mathrm{e}^{-\beta H_S^{\mathrm{ren}}}}{Z_{\mathrm{S}}^{\mathrm{ren}}}, \quad \text{with} \quad H_S^{\mathrm{ren}} = \frac{1}{2}\begin{pmatrix} \epsilon - \alpha_1 & 0 \\ 0 & -\epsilon - \alpha_2 \end{pmatrix}. \tag{3.4}$$

In this sense, the system energies $\pm\frac{1}{2}\epsilon$ are *renormalized* by $-\frac{1}{2}\alpha_j \propto -\lambda_j^2$, due to the interaction with the reservoir. Note though, that *the system is entangled with the reservoir in the equilibrium state $\rho_{\beta,\vec\lambda,0}$.*

The situation for the model with the two local reservoirs is analogous. The interacting dimer-reservoirs equilibrium state ($V = 0$) is given by

$$
\begin{aligned}
\rho_{\beta,\vec\lambda,0} &= \frac{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)}}{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)} + \mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}} \, |\varphi_1\rangle\langle\varphi_1| \otimes W^*\big(\lambda_1 g_1/(\mathrm{i}\omega)\big)\rho_{\mathrm{R}_1} W\big(\lambda_1 g_1/(\mathrm{i}\omega)\big) \otimes \rho_{\mathrm{R}_2} \\
&\quad + \frac{\mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}}{\mathrm{e}^{-\frac{\beta}{2}(\epsilon-\alpha_1)} + \mathrm{e}^{-\frac{\beta}{2}(-\epsilon-\alpha_2)}} \, |\varphi_2\rangle\langle\varphi_2| \otimes \rho_{\mathrm{R}_1} \otimes W^*\big(\lambda_2 g_2/(\mathrm{i}\omega)\big)\rho_{\mathrm{R}_2} W\big(\lambda_2 g_2/(\mathrm{i}\omega)\big).
\end{aligned} \tag{3.5}
$$

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By tracing out the reservoir in (3.5) we find again a dimer state of the form (3.4), with $\alpha_{1,2}$ given by (3.1).

We point out that if $\alpha_1 = \alpha_2$ (e.g. if $\lambda_1 = \lambda_2 = \lambda$ and $g_1 = g_2 = g$), then H_S^{ren} differs from H_S (with $V = 0$) just by a constant and the reduced dimer equilibrium state is the same for the coupled and the uncoupled system.

3.2 Relaxation and decoherence

In Section 4, we prove the following result.

Theorem 3.1 (Population dynamics, relaxation) *Let λ_1, λ_2 be arbitrary. There is a $V_0 > 0$ such that if $0 < |V| < V_0$, then*

$$p(t) = p_\infty + \mathrm{e}^{-\gamma t} \left(p(0) - p_\infty \right) + R(t), \tag{3.6}$$

where

$$p_\infty = \frac{\mathrm{e}^{-\frac{\beta}{2}(\epsilon - \alpha_1)}}{\mathrm{e}^{-\frac{\beta}{2}(\epsilon - \alpha_1)} + \mathrm{e}^{-\frac{\beta}{2}(-\epsilon - \alpha_2)}} + O(V) \tag{3.7}$$

is the level 1 population of the dimer density matrix at equilibrium coupled with the reservoir(s). Here $\alpha_{1,2}$ are the renormalization energies given in (3.1), and the relaxation rate γ is given by (2.25), for the model with the collective reservoir and that with the local ones, respectively. The remainder term $O(V)$ is independent of time t and $R(t)$ satisfies

$$R(0) = 0 \quad and \quad |R(t)| \leq C_1/t, \tag{3.8}$$

for some constant C_1.

Remark. The dynamical resonance theory of [13] which we use to prove the expansion (3.6) is set up so as to give a remainder that decays as $t \to \infty$. Instead, one could modify this theory to yield a remainder which is $O(V)$ for all times, but may not vanish at $t = \infty$. We do not explore this modification here.

We now discuss the decoherence properties of the dimer. The models with $V = 0$ can be solved exactly, see Section B.2. Namely,

$$[\rho_S(t)]_{12} = \mathrm{e}^{-\mathrm{i}t\hat{\epsilon}} \, \mathcal{D}(t) \, [\rho_S(0)]_{12}, \qquad (V = 0) \tag{3.9}$$

where $\hat{\epsilon}$ is given in (2.14) and

$$\mathcal{D}(t) = \begin{cases} \mathrm{e}^{-\frac{\mathrm{i}}{\pi}(\lambda_1^2 - \lambda_2^2)Q_1(t)} \mathrm{e}^{-\frac{1}{\pi}(\lambda_1 - \lambda_2)^2 Q_2(t)} & \text{(collective)} \\ \text{and} \\ \mathrm{e}^{-\frac{\mathrm{i}}{\pi}[\lambda_1^2 Q_1^{(1)}(t) - \lambda_2^2 Q_1^{(2)}(t)]} \mathrm{e}^{-\frac{1}{\pi}[\lambda_1^2 Q_2^{(1)}(t) + \lambda_2^2 Q_2^{(2)}(t)]} & \text{(local)} \end{cases} \tag{3.10}$$

for the collective and the local resevoirs models, respectively, with $Q_{1,2}(t)$ and $Q_{1,2}^{(j)}(t)$ given in (2.26) and (2.27). The following result is proven in Section B.2, see (B.13).

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Proposition 3.2 *We have*

$$\lim_{t\to\infty} \mathcal{D}(t) = e^{-\Gamma_\infty} \tag{3.11}$$

where

$$\Gamma_\infty = \begin{cases} \frac{1}{\pi}(\lambda_1 - \lambda_2)^2 \int_0^\infty \frac{J(\omega)}{\omega^2} \coth(\beta\omega/2)\mathrm{d}\omega & \text{(collective)} \\ \text{and} \\ \frac{1}{\pi}\lambda_1^2 \int_0^\infty \frac{J_1(\omega)}{\omega^2} \coth(\beta\omega/2)\mathrm{d}\omega + \frac{1}{\pi}\lambda_2^2 \int_0^\infty \frac{J_2(\omega)}{\omega^2} \coth(\beta\omega/2)\mathrm{d}\omega & \text{(local)} \end{cases} \tag{3.12}$$

for the collective and the local reservoirs models, respectively.

Remark. For spectral functions $J(\omega)$ of the form (2.8) we have

$$\Gamma_\infty = \infty \quad \Longleftrightarrow \quad p \le 0, \tag{3.13}$$

provided $\lambda_1 \ne \lambda_2$ (collective) and $\lambda_1, \lambda_2 \ne 0$ (local), the divergence of the integrals in (3.12) for $p \le 0$ stemming from a non-integrable singularity at low modes ($\omega \approx 0$).

We now introduce the *Lamb shift*,

$$x_{\mathrm{LS}} = \frac{V^2}{2} \lim_{r\to0_+} \tag{3.14}$$

$$\begin{cases} \int_0^\infty e^{-rt} \sin(\hat\epsilon t) \cos\left[\frac{(\lambda_1-\lambda_2)^2}{\pi} Q_1(t)\right] \exp\left[-\frac{(\lambda_1-\lambda_2)^2}{\pi} Q_2(t)\right]\mathrm{d}t & \text{(collective)} \\ \\ \int_0^\infty e^{-rt} \sin(\hat\epsilon t) \cos\left[\frac{\lambda_1^2}{\pi} Q_1^{(1)}(t) + \frac{\lambda_2^2}{\pi} Q_1^{(2)}(t)\right] \exp\left[-\frac{\lambda_1^2}{\pi} Q_2^{(1)}(t) - \frac{\lambda_2^2}{\pi} Q_2^{(2)}(t)\right]\mathrm{d}t & \text{(local)} \end{cases}$$

In Section 4, we prove the following result.

Theorem 3.3 (Decoherence) *Let λ_1, λ_2 be arbitrary. There is a $V_0 > 0$ such that if $0 < |V| < V_0$, then*

$$[\rho_{\mathrm{S}}(t)]_{12} = e^{-\Gamma_\infty} e^{-\gamma t/2} e^{-it(\hat\epsilon + x_{\mathrm{LS}})} [\rho_{\mathrm{S}}(0)]_{12} + O(V) + R(t), \tag{3.15}$$

where γ is given in (2.25) and x_{LS} is the Lamb shift (3.14). The term $O(V)$ is independent of time t and $R(t)$ satisfies

$$|R(t)| \le C_1 \quad \text{and} \quad |R(t)| \le C_2/t, \tag{3.16}$$

for some constants C_1, C_2.

3.3 Numerical simulations

The spectral functions of the collective and local environments are taken as in (2.28), with $p_1 = p_2 = p$ in the case of local reservoirs (the results obtained below can be generalized in a straightforward way for the case $p_1 \ne p_2$). In the numerical simulations, we have chosen a weakly coupled dimer based on two chlorophylls, $Chl^*a - Chl^*b$, in their excited states. The following parameters of the dimer were chosen,

$$\epsilon = 150ps^{-1} \approx 99meV \quad \text{and} \quad V = 25ps^{-1} \approx 16.5meV$$

(so $|V/\epsilon| \approx 0.17$), and the room temperature: $T = 25meV \approx 37.88ps^{-1}$ ($\beta \approx 0.026ps$).

Relaxation

It is convenient to define new dimensionless quantities

$$\varepsilon = \beta\epsilon, \quad \varepsilon_i^c = \beta\epsilon_{\text{col},i}, \quad \varepsilon_i^l = \beta\epsilon_{\text{loc},i} \quad i = 1,2 \quad \text{and} \quad \tau = t/\beta. \tag{3.17}$$

Using this notation, the relaxation rates (2.25) become

$$\gamma_{\text{col}} = \beta V^2 \int_0^\infty \cos\left[(\varepsilon - \frac{\varepsilon_1^c - \varepsilon_2^c}{2})\tau\right] \cos\left[\frac{\varepsilon_1^c + \varepsilon_2^c}{2}\mathcal{Q}_1(\tau)\right] \exp\left[-\frac{\varepsilon_1^c + \varepsilon_2^c}{2}\mathcal{Q}_2(\tau)\right] d\tau, \tag{3.18}$$

$$\gamma_{\text{loc}} = \beta V^2 \int_0^\infty \cos\left[(\varepsilon - \frac{\varepsilon_1^l - \varepsilon_2^l}{2})\tau\right] \cos\left[\frac{\varepsilon_1^l}{2}\mathcal{Q}_1^{(1)}(\tau) + \frac{\varepsilon_2^l}{2}\mathcal{Q}_1^{(2)}(\tau)\right]$$

$$\times \exp\left[-\frac{\varepsilon_1^l}{2}\mathcal{Q}_2^{(1)}(\tau) - \frac{\varepsilon_2^l}{2}\mathcal{Q}_2^{(2)}(\tau)\right] d\tau, \tag{3.19}$$

where we understand that a limit $r \to 0_+$ has to be performed (as in (2.25)), and where we have set $\mathcal{Q}_{1,2}(\tau) = Q_{1,2}(\tau)/(\beta\nu)$ and $\mathcal{Q}_{1,2}^{(i)}(\tau) = Q_{1,2}^{(i)}(\tau)/(\beta\nu_i)$ $(i = 1,2)$. We have,

$$\nu = \frac{A_p\eta^{2p+2}}{\beta^{2p+2}} \int_0^\infty z^{2p+1}e^{-z}dz, \tag{3.20}$$

$$\mathcal{Q}_1(\tau) = \frac{1}{\eta\Gamma(2p+2)} \int_0^\infty z^{2p}e^{-z}\sin((\eta\tau z))dz, \tag{3.21}$$

$$\mathcal{Q}_2(\tau) = \frac{1}{\eta\Gamma(2p+2)} \int_0^\infty z^{2p}e^{-z}(1 - \cos((\eta\tau z)))\coth(\eta z/2)dz, \tag{3.22}$$

where $\eta = \beta\omega_c$ and $z = \omega/\omega_c$.

Performing the integrations in (3.20)-(3.22), we obtain,

$$\nu = \frac{A_p\eta^{2p+2}\Gamma(2p+2)}{\beta^{2p+2}}, \tag{3.23}$$

$$\mathcal{Q}_1(\tau) = \frac{1}{(2p+1)\eta}\Im\left(\frac{1}{(1 - i\eta\tau)^{2p+1}}\right), \tag{3.24}$$

$$\mathcal{Q}_2(\tau) = \frac{1}{(2p+1)\eta}\Re(f(0) - f(\tau)), \qquad p > -1/2, \, p \neq 0. \tag{3.25}$$

Here,

$$f(\tau) = \frac{1}{\eta^{2p+1}}\left(\zeta\left(2p+1, \frac{1}{\eta} + i\tau\right) + \zeta\left(2p+1, \frac{1}{\eta} + 1 + i\tau\right)\right), \tag{3.26}$$

and $\zeta(s,q)$ denotes the Hurwitz ζ-function [28].

One can see that for $p > 0$ the function $\mathcal{Q}_2(\tau)$ is bounded from above by

$$\mathcal{Q}_0 = \lim_{\tau\to\infty}\mathcal{Q}_2(\tau) = \frac{1}{(2p+1)\eta^{2p+2}}\left(\zeta\left(2p+1, \frac{1}{\eta}\right) + \zeta\left(2p+1, \frac{1}{\eta}+1\right)\right). \tag{3.27}$$

Using the asymptotic properties of the ζ-function, we obtain

$$\mathcal{Q}_0 \approx \begin{cases} \dfrac{1}{(2p+1)p\eta^2}, & \eta \ll 1, \quad p > 0 \\ \dfrac{1}{(2p+1)\eta} + \dfrac{2\zeta(2p+1)}{(2p+1)\eta^{2p+2}} - \dfrac{2\zeta(2p+2)}{\eta^{2p+3}}, & \eta \gg 1, \quad p > 0 \end{cases} \tag{3.28}$$

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where $\zeta(s)$ is the Riemann zeta function, $\zeta(s) = \zeta(s, 1)$. One can estimate $\mathcal{Q}_2(\tau)$ as,

$$\mathcal{Q}_2(\tau) \approx \begin{cases} \tau^2 & \eta \ll 1, \eta\tau \ll 1 \; (p > -1/2) \\ \dfrac{(p+1)(2\zeta(2p+3, \frac{1}{\eta}) - \eta^{2p+3})\tau^2}{\eta^{2p+2}}, & \eta\tau \ll 1 \; (p > -1/2) \\ \dfrac{1}{(2p+1)\eta}\Re\left(1 - \dfrac{1}{(1+i\eta\tau)^{2p+1}}\right), & \eta \gg 1, \eta\tau \gg 1 \; (p > 0) \\ \dfrac{1}{(2p+1)p\eta^2}\Re\left(1 - \dfrac{1}{(1+i\eta\tau)^{2p}}\right), & \eta\tau \gg 1 \; (-1/2 < p < 0) \\ \dfrac{1}{(2p+1)p\eta^2}\Re\left(1 - \dfrac{1}{(1+i\eta\tau)^{2p}}\right), & \eta \ll 1, \tau > 0 \; (p > -1/2) \end{cases} \quad (3.29)$$

Similar considerations yield the asymptotic behavior for the function $\mathcal{Q}_1(\tau)$,

$$\mathcal{Q}_1(\tau) \approx \begin{cases} \tau, & \eta\tau \ll 1 \\ \dfrac{\tau \cos(\pi p)}{(2p+1)(\eta\tau)^{2p+2}} + \dfrac{\tau \sin(\pi p)}{(\eta\tau)^{2p+3}}, & \eta\tau \gg 1, \quad p > -1/2 \end{cases} \quad (3.30)$$

In Fig. 2, the functions, $\mathcal{Q}_1(\tau)$ and $\mathcal{Q}_2(\tau)$, are presented for various values of parameters, p and η. As one can see, in the high-temperature regime, $\eta \ll 1$, the conditions (2.52) and (2.54) are satisfied for $p \leq 0$, while for $p > 0$ a saturation of $\mathcal{Q}_2(\tau)$ at finite values ($\mathcal{Q}_2(\infty) < \infty$) takes place. The asymptotic behavior of the function $\mathcal{Q}_2(\tau)$ significantly influences the quantum coherence in the system.

Generalized Marcus limit

The relaxation rates in the Generalized Marcus limit are given in (2.35) and (2.41). In the new variables, they are

$$\gamma_{\text{col}} = \beta \left(\frac{V}{2}\right)^2 \sqrt{\frac{2\pi}{\varepsilon_1^c + \varepsilon_2^c}} \left\{ \exp\left[-\frac{(\varepsilon - \varepsilon_1^c)^2}{2(\varepsilon_1^c + \varepsilon_2^c)}\right] + \exp\left[-\frac{(\varepsilon + \varepsilon_2^c)^2}{2(\varepsilon_1^c + \varepsilon_2^c)}\right] \right\}, \quad (3.31)$$

$$\gamma_{\text{loc}} = \beta \left(\frac{V}{2}\right)^2 \sqrt{\frac{2\pi}{\varepsilon_1^l + \varepsilon_2^l}} \left\{ \exp\left[-\frac{(\varepsilon - \varepsilon_1^l)^2}{2(\varepsilon_1^l + \varepsilon_2^l)}\right] + \exp\left[-\frac{(\varepsilon + \varepsilon_2^l)^2}{2(\varepsilon_1^l + \varepsilon_2^l)}\right] \right\}. \quad (3.32)$$

In the case $\varepsilon_c = \varepsilon_1^c = \varepsilon_2^c$, or $\varepsilon_l = \varepsilon_1^l = \varepsilon_2^l$, they take the standard Marcus form (see also [38]),

$$\gamma_{\text{col,loc}} = \beta \left(\frac{V}{2}\right)^2 \sqrt{\frac{\pi}{\varepsilon_{c,l}}} \left\{ \exp\left[-\frac{(\varepsilon - \varepsilon_{c,l})^2}{4\varepsilon_{c,l}}\right] + \exp\left[-\frac{(\varepsilon + \varepsilon_{c,l})^2}{4\varepsilon_{c,l}}\right] \right\}, \quad (3.33)$$

for the collective and local reservoirs models, respectively.

In Figs. 3 and 4, we compare the ET rates obtained by numerical integration of (3.18) and (3.19), with the generalized Marcus formulas given by (3.31)-(3.33), corresponding to the high-temperature limit $\eta \ll 1$. All two-dimensional surfaces shown in Figs. 3 and 4 correspond to the exact Eqs. (3.18) and (3.19). Fig. 3(a) shows the high-temperature regime, $\eta = 0.1$. In this case, the rate $\gamma_{\text{col}}(x, y)$, obtained from the generalized Marcus formula (3.31), yields a surface that practically coincides with the surface defined $\gamma_{\text{col}}(x, y)$ obtained from the exact Eq. (3.18), for
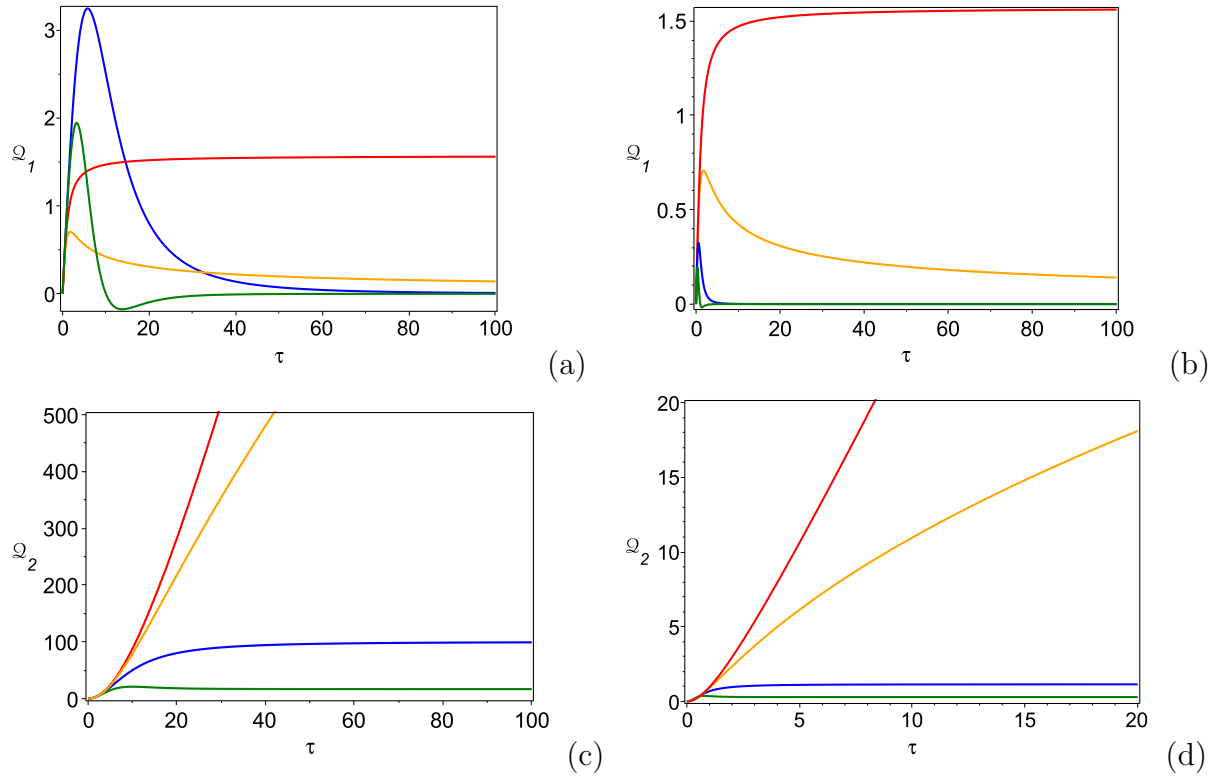
Figure 2: (Color online) The behavior of the functions $\mathcal{Q}_1(\tau)$, (3.21), in graphs (a,b) and $\mathcal{Q}_2(\tau)$, (3.22), in graphs (c,d). In (a,c): $\eta = 0.1$, in (b,d): $\eta = 1$. Parameters: $p = -1/4$ (orange curve), $p = -1/2 + 0$ (red curve), $p = 1/2$ (blue curve), $p = 3/2$ (green curve).
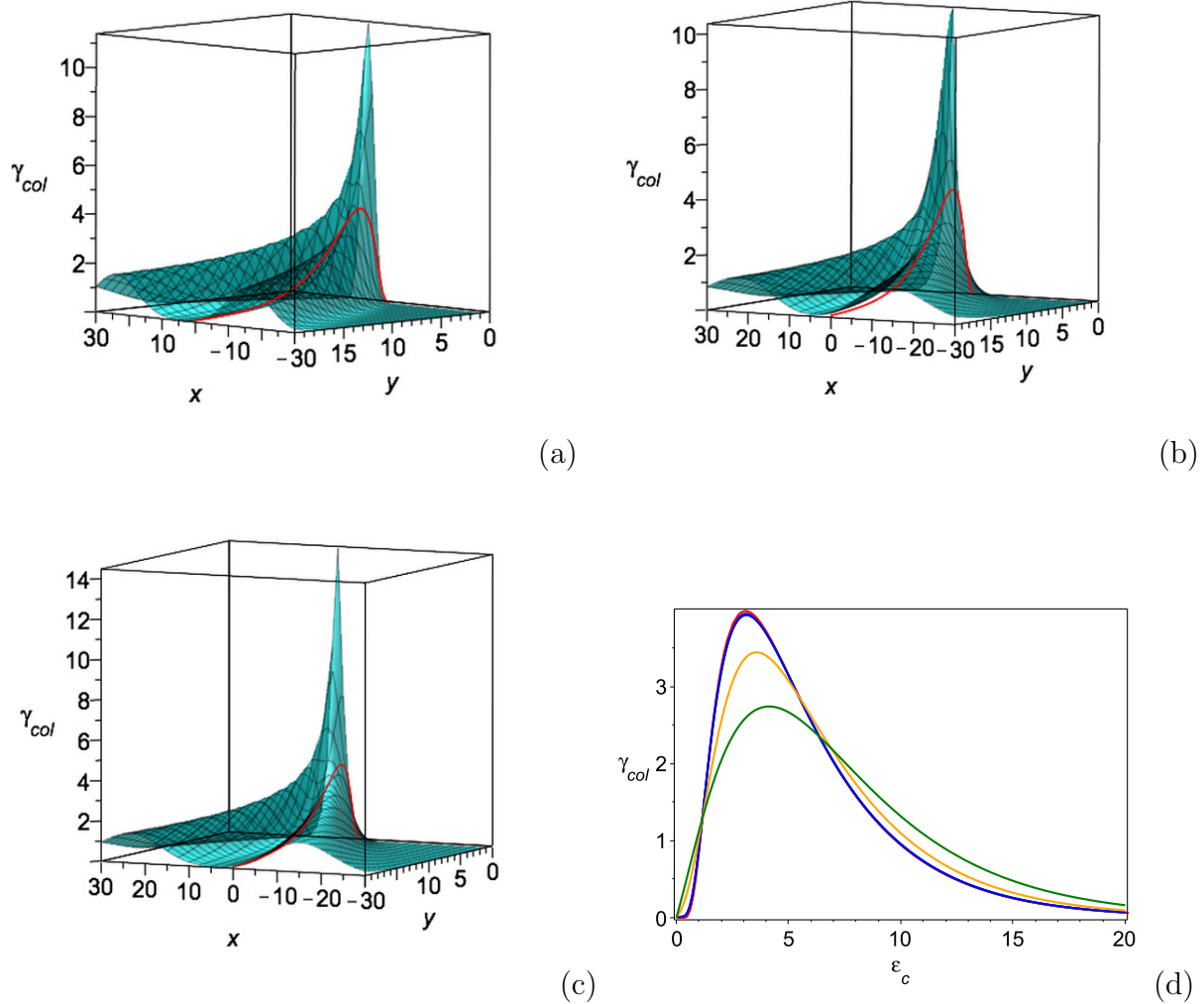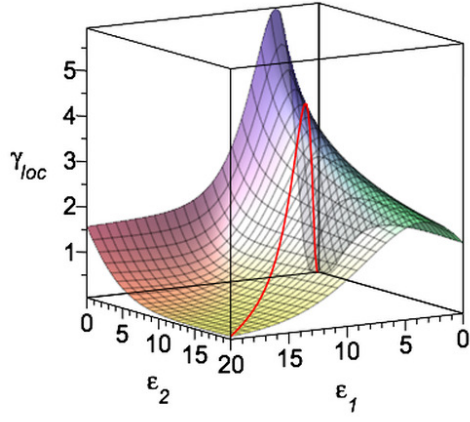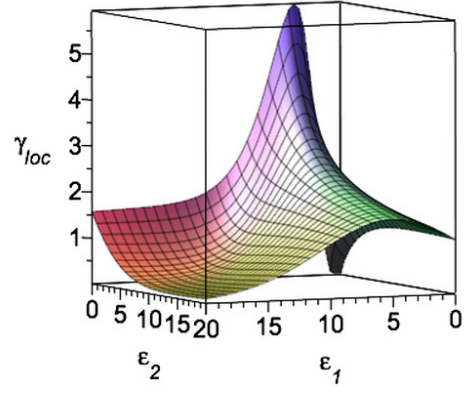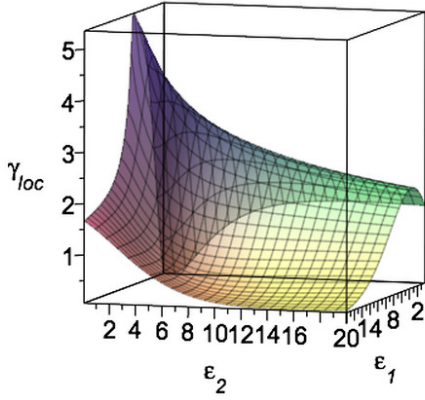
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Figure 3: (Color online) The ET rates for the collective environment, γ_{col}, given in (3.18), as a function of $x = (\varepsilon_1^c - \varepsilon_2^c)/2$ and $y = (\varepsilon_1^c + \varepsilon_2^c)/2$, γ_{col} is measured in ps^{-1}. The red curves correspond to the Marcus formula (3.33). (a) $\eta = 0.1$, $p = 1/2$; (b) $\eta = 1$, $p = 1/2$. (c) $\eta = 1$, $p = -1/4$; (d) $\eta = 0.1$, $p = 1/2$ (blue), $\eta = 1$, $p = 1/2$ (green), $\eta = 1$, $p = -1/4$ (orange).
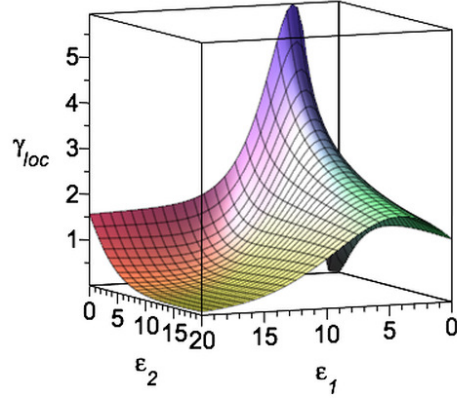
Figure 4: (Color online) The ET rates for local environments, γ_{loc}, given in (3.19), as a function of $\varepsilon_1 = \varepsilon_1^l$ and $\varepsilon_2 = \varepsilon_2^l$, where ε_1 and ε_2 are the reconstruction energies; γ_{loc} is measured in ps^{-1}. The red curve corresponds to the Marcus formula (3.32). (a) $p = 1/2$, $\eta_1 = \eta_2 = 0.1$; (b) $p = 1/2$, $\eta_1 = 0.1$, $\eta_2 = 1$; (c) $p = 1/2$, $\eta_1 = 1$, $\eta_2 = 0.1$; (d) $p = -1/4$, $\eta_1 = 0.1$, $\eta_2 = 1$.

all x, y. The large peak in Fig. 3(a) lies inside the parameter region for the guaranteed domain of applicability of the theory, namely, $\gamma_{\text{col}} \ll 2\sqrt{2\pi}(V/2)^2/\omega_c = 2\sqrt{2\pi}(25/2)^2/3.7\text{ps}^{-1} \approx 206\text{ps}^{-1}$, see (2.43). The values of γ_{col} for small values of y lie outside the domain for which we can guarantee that the generalized Marcus formula is approximating correctly the rate (c.f. (2.37)). So, in the numerical simulations of Fig. 3(a) we take $y \geq 1$. The red curves in Fig. 3 correspond to the standard Marcus ET rate, given by Eq. (3.33). As expected, the red curve in Fig. 3(a) lies on the surface $\gamma_{\text{col}}(x, y)$. The ET rates shown by the red curve in Fig. 3(a) (Marcus high-temperature regime, $\eta = 0.1$) are close to the experimental values reported in [10] ($\gamma_{\text{exp}} \approx 2\text{ps}^{-1}$). Still, the ET rates given by the surface but away from the red curve, corresponding to the generalized Marcus formula, can significantly exceed the values on the red curve.

In Fig. 3(b) and Fig. 3(c) we take $\eta = 1$, which does not correspond to the high-temperature regime any longer. Our numerical simulations demonstrate that the generalized Marcus formula for γ_{col}, given by Eq. (3.31), does not work in this case. In particular, the red curves in Fig. 3(b) and Fig. 3(c) partly lie outside the two-dimensional surfaces corresponding to the exact formulas. The difference between the exact results for γ_{col} and the generalized Marcus formula is shown in Fig. 3(d), for the dependence $\gamma_{\text{col}}(\varepsilon_c)$, where $\varepsilon_c = \varepsilon_1^c = \varepsilon_2^c$. As one can see, only the blue curve, corresponding to the exact formula in the high-temperature regime ($\eta = 0.1$), practically coincides with the Marcus formula (3.33).

In Fig. 4, similar results (to those presented in Fig. 3) are shown for $\gamma_{\text{loc}}(\varepsilon_1, \varepsilon_2)$. The two-dimensional surfaces correspond in this case to the exact formulass of Eq. (3.19). The high-temperature regime is shown in Fig. 4(a) ($\eta_1 = \eta_2 = 0.1$). In this case, the generalized Marcus formula, given by Eq. (3.32), practically describes the exact result in the whole region of the reconstruction energies, $(\varepsilon_1, \varepsilon_2)$. In particular, the red curve in Fig. 4(a) (corresponding to Eq. (3.33)) lies on the two-dimensional surface, $\gamma_{\text{loc}}(\varepsilon_1, \varepsilon_2)$. Similar to the case of the collective environment, the ET rates, γ_{loc}, of the generalized Marcus formula (3.32), can exceed the ET rates corresponding to the standard Marcus formula given by Eq. (3.33). The results of our numerical simulations of the exact Eq. (3.19) (shown in Figs. 4(b,c,d)) demonstrate that outside the high-temperature regime ($\eta \ll 1$), the generalized Marcus formula, given by Eq. (3.32), cannot be used. (However, we do have the correct expressions for γ_{col}, γ_{loc}, even in this regime, c.f. (3.31)-(3.33).)

Decoherence at $V = 0$

For $V = 0$ there is no relaxation, only decoherence in the energy basis occurs [29]. The saturated value of the non-diagonal reduced density matrix elements is characterized by the factor $e^{-\Gamma_\infty}$ given in (3.12). In the variables (3.17) we have

$$\Gamma_\infty = \lim_{\tau \to \infty} \Gamma(\tau), \qquad \text{where} \qquad \Gamma(\tau) = \begin{cases} \dfrac{(\varepsilon_1^c + \varepsilon_2^c)}{2}\mathcal{Q}_2(\tau) & \text{(collective)} \\[2ex] \dfrac{\varepsilon_1^l}{2}\mathcal{Q}_2^{(1)}(\tau) + \dfrac{\varepsilon_2^l}{2}\mathcal{Q}_2^{(2)}(\tau) & \text{(local)} \end{cases} \tag{3.34}$$

As one can see from Eq. (3.34), the asymptotic behavior of the function $\mathcal{Q}_2(\tau)$ significantly effects the quantum coherence in the system. We plot the function $\mathcal{Q}_2(\tau, \eta)$ in Fig. 5 (see also Fig. 2). One can see that in the high-temperature regime, $\eta \ll 1$, $\mathcal{Q}_2(\tau)$ increases very fast
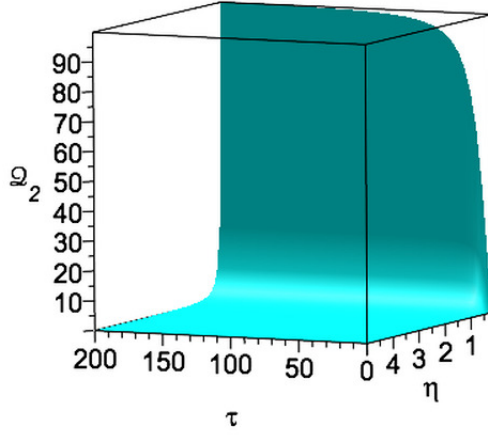
Figure 5: (Color online) The dependence $\mathcal{Q}_2$ on τ and η ($p = 1/2$, $0.1 \leq \eta \leq 5$).

when τ increases. Hence one expects strong decoherence in this case. In the regime of partial phase decoherence, $p > 0$, we can use the asymptotic formulas (3.27) to obtain

$$
\Gamma_\infty = \begin{cases} \dfrac{(\varepsilon_1^c + \varepsilon_2^c)}{2} \mathcal{Q}_0 & \text{(collective)} \\[2ex] \dfrac{\varepsilon_1^l}{2} \mathcal{Q}_0^{(1)} + \dfrac{\varepsilon_2^l}{2} \mathcal{Q}_0^{(2)} & \text{(local)} \end{cases}
\tag{3.35}
$$

Here,

$$
\mathcal{Q}_0 = \frac{1}{(2p+1)\eta^{2p+2}} \left(\zeta\left(2p+1, \frac{1}{\eta}\right) + \zeta\left(2p+1, \frac{1}{\eta}+1\right) \right),
\tag{3.36}
$$

for the collective environment model and

$$
\mathcal{Q}_0^i = \frac{1}{(2p+1)\eta_i^{2p+2}} \left(\zeta\left(2p+1, \frac{1}{\eta_i}\right) + \zeta\left(2p+1, \frac{1}{\eta_i}+1\right) \right), \quad i = 1, 2,
\tag{3.37}
$$

for the local environments model.

Fig. 6 shows the decoherence function $\mathrm{e}^{-\Gamma(\tau,\eta)}$ for both collective and local environments, and for $p > 0$. Quantum coherence in this case ($p > 0$) survives for large times (for all times if $V = 0$). The level of quantum coherence strongly depends on the value of η the for collective environment and on η_1 and η_2 for the local environments. Namely, quantum coherence is strong for η, $\eta_{1,2}$ not too small. Indeed, for $\eta = 0.1$ (blue curve in Fig. 6b), coherence is very small at large times.

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(a)

(b)

(c)

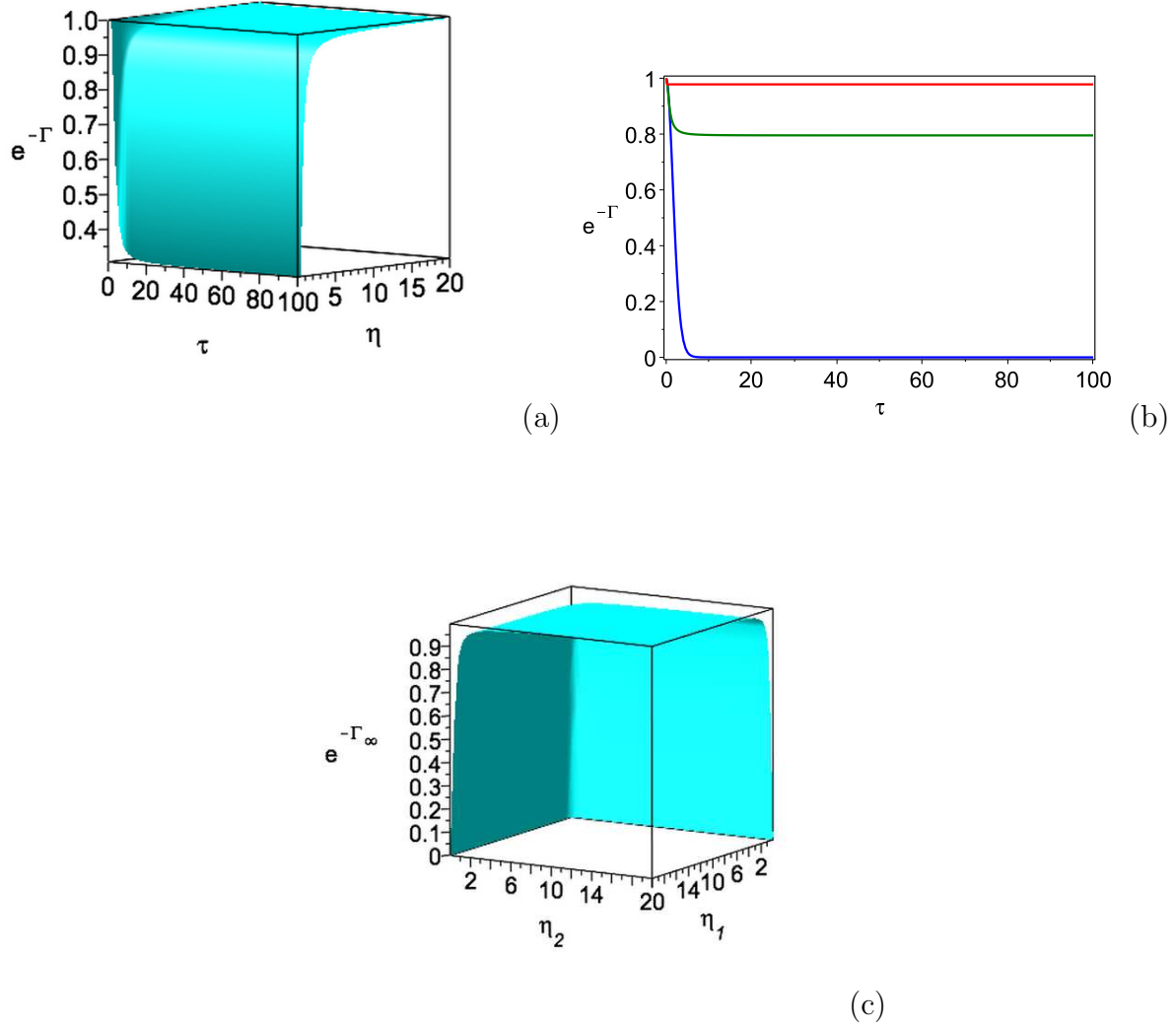Figure 6: (Color online) The decoherence function $\mathrm{e}^{-\Gamma(\tau)}$, with $\Gamma(\tau)$ given in (3.34), as a function of τ and η. (a,b) collective environment; (b) $\eta = 0.1$ (blue curve), $\eta = 1$ (green curve), $\eta = 5$ (red curve); $p = 1/2$, $\varepsilon = 0.2$. (c) $\mathrm{e}^{-\Gamma_\infty}$ for local environments: $p = 1/2$, $\varepsilon_1 = \varepsilon_2 = 0.1$.

4 Dynamical resonance theory

4.1 The mathematical setup

The description of a small system (dimer) coupled to infinitely extended Bose reservoirs, or continuous modes oscillator reservoirs, is phrased mathematically in terms of the language of W^*-dynamical systems. We note that we start off with a reservoir having continuous modes. Often in the physics literature, one first considers a reservoir of finitely many modes (quantized for instance because confined to a finite volume). Then one performs calculations, reaches expressions for, say, the relaxation rates, and finally takes the limit of continuous modes in the end. The arguments leading to expressions of relaxation rates in this way (the procedure being called the "time-dependent perturbation theory"), are often based on taking large-time limits ($t \to \infty$). It is not clear if these arguments are really valid since in general, performing first the large time limit and then the continuous modes limit (or, infinite volume limit) is not the same as performing the limits in the opposite order (as taking first $t \to \infty$ at discrete modes or finite volume depends on 'boundary effects'). Thus, for a rigorous analysis, we first perform the infinite volume limit and get results which hold *for all times* $t \geq 0$. This approach has been fruitful in many situations recently [18, 13, 14, 19, 20, 21, 22].

The total system is a W^*-dynamical system $(\mathcal{H}, \mathfrak{M}, \alpha)$, where $\mathfrak{M}$ is a von Neumann algebra of observables acting on a Hilbert space $\mathcal{H}$ and where α^t is a group of $*$automorphisms of $\mathfrak{M}$. The "positive temperature Hilbert space" is given by

$$\mathcal{H} = \mathbb{C}^2 \otimes \mathbb{C}^2 \otimes \mathcal{F}_\beta \quad \text{or} \quad \mathcal{H} = \mathbb{C}^2 \otimes \mathbb{C}^2 \otimes \mathcal{F}_\beta \otimes \mathcal{F}_\beta, \tag{4.1}$$

depending on whether we have one or two reservoirs. Here, $\mathcal{F}_\beta$ is the Fock space

$$\mathcal{F}_\beta = \bigoplus_{n \geq 0} L^2_{\text{sym}}((\mathbb{R} \times S^2)^n, (du \times d\Sigma)^n). \tag{4.2}$$

It differs from the 'usual zero-temperature' Fock space $\oplus_{n \geq 0} L^2_{\text{sym}}((\mathbb{R}^{3n}, d^{3n}k))$ in that the single-particle space at positive temperature is the 'glued' space $L^2(\mathbb{R} \times S^2, du \times d\Sigma)$ [11] ($d\Sigma$ is the uniform measure on S^2). $\mathcal{F}_\beta$ carries a representation of the CCR (canonical commutation relation) algebra. The represented Weyl operators are given by $W(f_\beta) = \mathrm{e}^{i\phi(f_\beta)}$, where $\phi(f_\beta) = \frac{1}{\sqrt{2}}(a^*(f_\beta) + a(f_\beta))$. Here, $a^*(f_\beta)$ and $a(f_\beta)$ denote creation and annihilation operators on $\mathcal{F}_\beta$, smoothed out with the function

$$f_\beta(u, \Sigma) = \sqrt{\frac{u}{1 - e^{-\beta u}}} \, |u|^{1/2} \begin{cases} f(u, \Sigma), & u \geq 0 \\ -\overline{f}(-u, \Sigma), & u < 0 \end{cases} \tag{4.3}$$

belonging to $L^2(\mathbb{R} \times S^2, du \times d\Sigma)$. It is easy to see that the CCR are satisfied, namely,

$$W(f_\beta)W(g_\beta) = e^{-\frac{i}{2}\mathrm{Im}\langle f, g\rangle} W(f_\beta + g_\beta). \tag{4.4}$$

The vacuum vector $\Omega \in \mathcal{F}_\beta$ represents the infinite-volume equilibrium state of the free Bose field, determined by the formula

$$\langle \Omega, W(f_\beta)\Omega \rangle = \exp\left\{ -\tfrac{1}{4} \langle f, \coth(\beta|k|/2)f\rangle \right\}. \tag{4.5}$$

The CCR algebra is represented on (4.2) as $W(f) \mapsto W(f_\beta)$, for $f \in L^2(\mathbb{R}^3)$ such that $\langle f, \coth(\beta|k|/2)f \rangle < \infty$. This representation was first derived by Araki and Woods [2]. We denote the von Neumann algebra of the represented Weyl operators by $\mathcal{W}_\beta$.

The doubled spin Hilbert space in (4.1) allows to represent any (pure or mixed) state of the two-level system by a vector, again by the GNS construction. This construction is also known as the *Liouville description* [25] and goes as follows. Let ρ be a density matrix on $\mathbb{C}^2$. When diagonalized it takes the form $\rho = \sum_i p_i |\chi_i\rangle\langle\chi_i|$, to which we associate the vector $\Psi_\rho = \sum_i \sqrt{p_i} \chi_i \otimes \overline{\chi}_i \in \mathbb{C}^2 \otimes \mathbb{C}^2$ (complex conjugation in any fixed basis – we will choose the eigenbasis of H_S, (2.11)). Then $\mathrm{Tr}(\rho A) = \langle \Psi_\rho, (A \otimes \mathbb{1}_S)\Psi_\rho \rangle$ for all $A \in \mathcal{B}(\mathbb{C}^2)$ and where $\mathbb{1}_S$ is the identity in $\mathbb{C}^2$. This is the GNS representation of the state given by ρ [4, 21].

The von Neumann algebra of observables of the total system is

$$\mathfrak{M} = \mathcal{B}(\mathbb{C}^2) \otimes \mathbb{1}_S \otimes \mathcal{W}_\beta \subset \mathcal{B}(\mathcal{H}). \tag{4.6}$$

The modular conjugation J is the antilinear operator defined by

$$J(A \otimes \mathbb{1}_S \otimes W(f_\beta(u, \Sigma)))J = \mathbb{1}_S \otimes \overline{A} \otimes W(\overline{f}_\beta(-u, \Sigma)), \tag{4.7}$$

where $\overline{A}$ is the matrix obtained from A by taking entrywise complex conjugation (matrices are represented in the eigenbasis of H_S). Note that by (4.3), we have $\overline{f}_\beta(-u, \Sigma) = -e^{-\beta u/2} f_\beta(u, \Sigma)$. By the Tomita-Takesaki theorem [4], conjugation by J maps the von Neumann algebra of observables (4.6) into its commutant. That is, V and JVJ commute for any $V \in \mathfrak{M}$.

The dynamics of the spin-boson system is given by

$$\alpha^t(A) = \mathrm{e}^{\mathrm{i}tL} A \mathrm{e}^{-\mathrm{i}tL}, \qquad A \in \mathfrak{M}. \tag{4.8}$$

It is generated by the self-adjoint Liouville operator acting on $\mathcal{H}$, associated to the Hamiltonian (2.1). For the single reservoir model,

$$L_{\mathrm{col}} = L_S + L_R + I_{\mathrm{col}} - JI_{\mathrm{col}}J, \tag{4.9}$$

where

$$L_S = \frac{1}{2}\begin{pmatrix} \varepsilon & V \\ V & -\varepsilon \end{pmatrix} \otimes \mathbb{1}_S - \mathbb{1}_S \otimes \frac{1}{2}\begin{pmatrix} \varepsilon & V \\ V & -\varepsilon \end{pmatrix} \tag{4.10}$$

$$L_R = \mathrm{d}\Gamma(u) \tag{4.11}$$

$$I_{\mathrm{col}} = \left(\lambda_1 P_1 + \lambda_2 P_2\right) \otimes \mathbb{1}_S \otimes \phi(g_\beta), \tag{4.12}$$

where $\mathrm{d}\Gamma(u) = \int u a^*(u, \Sigma) a(u, \Sigma) \mathrm{d}u \mathrm{d}\Sigma$ is the second quantization of the operator of multiplication by the radial variable u, $\phi(g_\beta)$ is the represented field operator and

$$P_1 = |\varphi_1\rangle\langle\varphi_1| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \qquad P_2 = |\varphi_2\rangle\langle\varphi_2| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4.13}$$

Similarly, the Liouvillian associated to the Hamiltonian (2.3) is

$$L_{\mathrm{loc}} = L_S + L_{R_1} + L_{R_2} + I_{\mathrm{loc}} - JI_{\mathrm{loc}}J, \tag{4.14}$$

with L_S given as in (4.10), the $L_{R_{1,2}}$ as in (4.11) (on their individual reservoir spaces) and

$$I_{\mathrm{loc}} = \lambda_1 P_1 \otimes \mathbb{1}_S \otimes \phi_1(g_1) + \lambda_2 P_2 \otimes \mathbb{1}_S \otimes \phi_2(g_2). \tag{4.15}$$

It is convenient to transform the Liouvillians unitarily by a "polaron transformation" [15, 14].

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Proposition 4.1 (Unitarily transformed Liouvillians)

(1) Define the unitaries $u = \mathrm{e}^{\mathrm{i}[P_1 \otimes \mathbb{1}_\mathrm{S} \otimes \phi(f_1) + P_2 \otimes \mathbb{1}_\mathrm{S} \otimes \phi(f_2)]}$ *and* $U = uJuJ$, *where*

$$f_{1,2} = (-\mathrm{i}\lambda_{1,2}\, g/\omega)_\beta. \tag{4.16}$$

Then

$$\widetilde{L}_\mathrm{col} := U L_\mathrm{col} U^* = L_\mathrm{S}^\mathrm{ren} + L_\mathrm{R} + \widetilde{I}_\mathrm{col}, \tag{4.17}$$

where

$$L_\mathrm{S}^\mathrm{ren} = H_\mathrm{S}^\mathrm{ren} \otimes \mathbb{1}_\mathrm{S} - \mathbb{1}_\mathrm{S} \otimes H_\mathrm{S}^\mathrm{ren}, \qquad H_\mathrm{S}^\mathrm{ren} = \frac{1}{2} \begin{pmatrix} \epsilon - \alpha_1 & 0 \\ 0 & -\epsilon - \alpha_2 \end{pmatrix} \tag{4.18}$$

with renormalization energies $\alpha_{1,2} = \lambda_{1,2}^2 \|g/\sqrt{\omega}\|_2^2$. *The transformed interaction is*

$$\widetilde{I}_\mathrm{col} = \frac{V}{2}\Big[\sigma_+ \otimes \mathbb{1}_\mathrm{S} \otimes W\left((\frac{\lambda_1 - \lambda_2}{\mathrm{i}\omega}g)_\beta\right) - \mathbb{1}_\mathrm{S} \otimes \sigma_+ \otimes JW\left((\frac{\lambda_1 - \lambda_2}{\mathrm{i}\omega}g)_\beta\right)J + \mathrm{h.c.}\Big], \tag{4.19}$$

where

$$\sigma_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}.$$

(2) Define the unitaries $u = \mathrm{e}^{\mathrm{i}[P_1 \otimes \mathbb{1}_\mathrm{S} \otimes \phi_1(f_1) + P_2 \otimes \mathbb{1}_\mathrm{S} \otimes \phi_2(f_2)]}$ *and* $U = uJuJ$, *where*

$$f_{1,2} = (-\mathrm{i}\lambda_{1,2}g_{1,2}/\omega)_\beta. \tag{4.20}$$

Then

$$\widetilde{L}_\mathrm{loc} := U L_\mathrm{loc} U^* = L_\mathrm{S}^\mathrm{ren} + L_{\mathrm{R}_1} + L_{\mathrm{R}_2} + \widetilde{I}_\mathrm{loc}, \tag{4.21}$$

where $L_\mathrm{S}^\mathrm{ren}$ *is given as in* (4.18) *with renormalization energies* $\alpha_{1,2} = \lambda_{1,2}^2 \|g_{1,2}/\sqrt{\omega}\|_2^2$. *The transformed interaction is*

$$\begin{aligned}
\widetilde{I}_\mathrm{loc} =\ & \frac{V}{2}\Big[\sigma_+ \otimes \mathbb{1}_\mathrm{S} \otimes W_1\left((\frac{\lambda_1 g_1}{\mathrm{i}\omega})_\beta\right) \otimes W_2^*\left((\frac{\lambda_2 g_2}{\mathrm{i}\omega})_\beta\right) \\
& -\mathbb{1}_\mathrm{S} \otimes \sigma_+ \otimes JW_1\left((\frac{\lambda_1 g_1}{\mathrm{i}\omega})_\beta\right)J \otimes JW_2^*\left((\frac{\lambda_2 g_2}{\mathrm{i}\omega})_\beta\right)J + \mathrm{h.c.}\Big].
\end{aligned} \tag{4.22}$$

Remarks. **1.** For a function $h(k)$, $k \in \mathbb{R}^3$, we have $\|h\|_2^2 = \int_{\mathbb{R}^3} |h(k)|^2 \mathrm{d}^3 k$.

2. If $\lambda_1 = \lambda_2$ (and $g_1 = g_2$ in the case of local reservoirs), then $L_\mathrm{S}^\mathrm{ren} = L_\mathrm{S}$.

3. Sometimes the following expressions for u are useful. In the case of the single collective reservoir, $u = P_1 \otimes \mathbb{1}_\mathrm{S} \otimes W(f_1) + P_2 \otimes \mathbb{1}_\mathrm{S} \otimes W(f_2)$. In the case of the two local reservoirs, $u = P_1 \otimes \mathbb{1}_\mathrm{S} \otimes W_1(f_1) + P_2 \otimes \mathbb{1}_\mathrm{S} \otimes W_2(f_2)$.

The proof of Proposition 4.1 is simply a calculation, based on the relations

$$W(f)L_\mathrm{R}W(f)^* = L_\mathrm{R} - \varphi(\mathrm{i}\omega f) + \tfrac{1}{2}\|\sqrt{\omega}f\|_2^2 \tag{4.23}$$

and

$$W(f)\varphi(g)W(f)^* = \varphi(g) - \mathrm{Im}\,\langle f, g\rangle. \tag{4.24}$$

4.2 Dynamics

4.2.1 Resonance expansion of the propagator

Let ψ_0 be the initial state (represented as a vector in the GNS Hilbert space). The expectation of a (represented) observable A (of the dimer and/or the reservoir(s)) at time t is

$$\langle A \rangle_t = \left\langle \psi_0, \mathrm{e}^{\mathrm{i}tL} A \mathrm{e}^{-\mathrm{i}tL} \psi_0 \right\rangle. \tag{4.25}$$

Since $\Omega_{\beta,\vec{\lambda},V}$ is separating (see [4]), there exists an operator B from the commutant algebra (commuting with all observables), s.t.

$$\psi_0 = B\Omega_{\beta,\vec{\lambda},V}. \tag{4.26}$$

Using relation (4.26) together with the fact that B commutes with $\mathrm{e}^{\mathrm{i}tL} A \mathrm{e}^{-\mathrm{i}tL}$ and the invariance $\mathrm{e}^{\mathrm{i}tL}\Omega_{\beta,\vec{\lambda},V} = \Omega_{\beta,\vec{\lambda},V}$ gives

$$\langle A \rangle_t = \left\langle \psi_0, B\mathrm{e}^{\mathrm{i}tL} A \Omega_{\beta,\vec{\lambda},V} \right\rangle. \tag{4.27}$$

We now use the unitary transformation U described in Proposition 4.1,

$$\langle A \rangle_t = \left\langle \psi_0, BU^* \mathrm{e}^{\mathrm{i}t\widetilde{L}} U A \Omega_{\beta,\vec{\lambda},V} \right\rangle, \tag{4.28}$$

where $\widetilde{L}$ is $\widetilde{L}_{\mathrm{col}}$ or $\widetilde{L}_{\mathrm{loc}}$ (see (4.17), (4.21)), depending on the model considered. (4.28) has the following resonance expansion, which follows from a general resonance expansion of propagators proven in [13]. Set, for ease of notation,

$$\Psi_1 = UB^*\psi_0 \quad \text{and} \quad \Psi_2 = UA\Omega_{\beta,\vec{\lambda},V}. \tag{4.29}$$

Then there is a $V_0 > 0$ s.t. for all $0 < |V| < V_0$, and all $t > 0$,

$$\left\langle \Psi_1, \mathrm{e}^{\mathrm{i}t\widetilde{L}}\Psi_2 \right\rangle = \omega_{\beta,\vec{\lambda},V}(A) \tag{4.30}$$

$$+ \left\langle \Psi_1, \left[\mathrm{e}^{-\gamma t}\Pi_0 + \mathrm{e}^{-\gamma t/2}\ \mathrm{e}^{\mathrm{i}t(\hat{\epsilon}+x_{\mathrm{LS}})}\Pi_+ + \mathrm{e}^{-\gamma t/2}\ \mathrm{e}^{-\mathrm{i}t(\hat{\epsilon}+x_{\mathrm{LS}})}\Pi_- \right] \Psi_2 \right\rangle + R(t).$$

Here, $\omega_{\beta,\vec{\lambda},V}$ is the coupled dimer-reservoir(s) equilibrium state. The "decay rate" is given by

$$\gamma = \gamma_{\mathrm{col}} + O(V^4) \quad \text{or} \quad \gamma = \gamma_{\mathrm{loc}} + O(V^4) \tag{4.31}$$

depending on whether we consider the model with the collective reservoir or the local ones, and where γ_{col}, γ_{loc} are given by (2.25). The quantity $x_{\mathrm{LS}} \in \mathbb{R}$ is the "Lamb shift". Moreover, the resonance projections are

$$\Pi_0 = \frac{1}{1 + \mathrm{e}^{-\beta\hat{\epsilon}}} |\varphi_{11} - \mathrm{e}^{-\beta\hat{\epsilon}/2}\varphi_{22}\rangle\langle\varphi_{11} - \mathrm{e}^{-\beta\hat{\epsilon}/2}\varphi_{22}| \otimes P_{\mathrm{R}} + O(V), \tag{4.32}$$

$$\Pi_+ = |\varphi_{12}\rangle\langle\varphi_{12}| \otimes P_{\mathrm{R}} + O(V), \tag{4.33}$$

$$\Pi_- = |\varphi_{21}\rangle\langle\varphi_{21}| \otimes P_{\mathrm{R}} + O(V), \tag{4.34}$$

where $\varphi_{ij} = \varphi_i \otimes \varphi_j$ (see also (2.11)) and

$$P_{\mathrm{R}} = |\Omega_{\mathrm{R}_1}\rangle\langle\Omega_{\mathrm{R}_1}| \quad \text{or} \quad P_{\mathrm{R}} = |\Omega_{\mathrm{R}_1}\rangle\langle\Omega_{\mathrm{R}_1}| \otimes |\Omega_{\mathrm{R}_2}\rangle\langle\Omega_{\mathrm{R}_2}|, \tag{4.35}$$

(projection onto the vacua of the reservoirs), depending on whether we consider the collective or local reservoirs models. The decay rates and Lamb shifts are (to lowest order in V) the real and imaginary parts of *level shift operators* which describe the perturbative movement of eigenvalues of $\widetilde{L}$ for small V. We calculate them explicitly in Appendix A.

The remainder $R(t)$ in (4.30) satisfies the following bounds: there are constants C_1 and C_2 (independent of t and V), such that for all $t > 0$,

$$|R(t)| \leq \frac{C_1}{t}, \quad |R(t)| \leq C_2. \tag{4.36}$$

Remark. To prove the expansion (4.30) one needs some regularity of the form factors g, $g_{1,2}$ appearing in (2.1) and (2.3). We explain them in Section C.

4.2.2 Effective dynamics

Define the operators D_j, $j = 0, \pm$, belonging to the algebra of observables of the joint dimer-reservoir(s) system, as follows.

(1) For the model with the single collective reservoir,

$$
\begin{aligned}
D_0 &= \mathrm{e}^{\beta\hat{\epsilon}/2}|\varphi_1\rangle\langle\varphi_1| \otimes \mathbb{1}_\mathrm{S} \otimes \mathbb{1}_\mathrm{R} - \mathrm{e}^{-\beta\hat{\epsilon}/2}|\varphi_2\rangle\langle\varphi_2| \otimes \mathbb{1}_\mathrm{S} \otimes \mathbb{1}_\mathrm{R} \\
D_+ &= \sqrt{1 + \mathrm{e}^{-\beta\hat{\epsilon}}}\,|\varphi_1\rangle\langle\varphi_2| \otimes \mathbb{1}_\mathrm{S} \otimes W^*(f_1)W(f_2) \\
D_- &= \mathrm{e}^{\beta\hat{\epsilon}/2}\sqrt{1 + \mathrm{e}^{-\beta\hat{\epsilon}}}\,|\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_\mathrm{S} \otimes W^*(f_2)W(f_1).
\end{aligned}
\tag{4.37}
$$

(Recall the definition (4.16) of $f_{1,2}$.)

(2) For the model with the two local reservoirs,

$$
\begin{aligned}
D_0 &= \mathrm{e}^{\beta\hat{\epsilon}/2}|\varphi_1\rangle\langle\varphi_1| \otimes \mathbb{1}_\mathrm{S} \otimes \mathbb{1}_{\mathrm{R}_1} \otimes \mathbb{1}_{\mathrm{R}_2} - \mathrm{e}^{-\beta\hat{\epsilon}/2}|\varphi_2\rangle\langle\varphi_2| \otimes \mathbb{1}_\mathrm{S} \otimes \mathbb{1}_{\mathrm{R}_1} \otimes \mathbb{1}_{\mathrm{R}_2} \\
D_+ &= \sqrt{1 + \mathrm{e}^{-\beta\hat{\epsilon}}}\,|\varphi_1\rangle\langle\varphi_2| \otimes \mathbb{1}_\mathrm{S} \otimes W^*(f_1) \otimes W(f_2) \\
D_- &= \mathrm{e}^{\beta\hat{\epsilon}/2}\sqrt{1 + \mathrm{e}^{-\beta\hat{\epsilon}}}\,|\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_\mathrm{S} \otimes W(f_1) \otimes W^*(f_2).
\end{aligned}
\tag{4.38}
$$

(Recall the definition (4.20) of $f_{1,2}$.)

The main result of this section is the following representation for the dynamics.

Theorem 4.2 *Let ω_0 be the initial dimer-reservoir(s) state and let A be a dimer-reservoir(s) observable. Then*

$$\langle A\rangle_t = \omega_{\beta,\vec{\lambda},V}(A) + \sum_{j=0,\pm} \mathrm{e}^{\mathrm{i}ta_j}\,\omega_0(D_j)\,\omega_{\beta,\vec{\lambda},0}(D_j^* A) + R(t), \tag{4.39}$$

where $\omega_{\beta,\vec{\lambda},V}$ is the dimer-reservoir(s) equilibrium state, $R(t)$ satisfies (4.36) and

$$
a_j = \begin{cases} \mathrm{i}\gamma & j = 0, \\ \mathrm{i}\gamma/2 \pm (\hat{\epsilon} + x_\mathrm{LS}) & j = \pm \end{cases}
\tag{4.40}
$$

where $\gamma = \gamma_\mathrm{col}$ or $\gamma = \gamma_\mathrm{loc}$ given in (2.25) and x_LS is the Lamb shift (3.14).

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Proof of Theorem 4.2.

We use the expansion (4.30). The following result follows from an easy calculation combining (4.32)-(4.34) with the definition of the unitary U given in Proposition 4.1.

Lemma 4.3 *The projections Π_j, $j = 0, \pm$, given in (4.32)-(4.34) have the form*

$$U^* \Pi_j U = |X_j\rangle\langle X_j| + O(V), \tag{4.41}$$

where the vectors X_j are as follows.

(1) *For the model with the collective reservoir, we have*

$$
\begin{aligned}
X_0 &= \frac{1}{\sqrt{1 + e^{-\beta\hat\epsilon}}} \left(\varphi_{11} \otimes W^*(f_1) J W^*(f_1) J \Omega_{\mathrm{R}} - e^{-\beta\hat\epsilon/2} \varphi_{22} \otimes W^*(f_2) J W^*(f_2) J \Omega_{\mathrm{R}} \right) \\
X_+ &= \varphi_{12} \otimes W^*(f_1) J W^*(f_2) J \Omega_{\mathrm{R}} \\
X_- &= \varphi_{21} \otimes W^*(f_2) J W^*(f_1) J \Omega_{\mathrm{R}}
\end{aligned}
\tag{4.42}
$$

(2) *For the model with the two local reservoirs, we have*

$$
\begin{aligned}
X_0 &= \frac{1}{\sqrt{1 + e^{-\beta\hat\epsilon}}} \big(\varphi_{11} \otimes W_1^*(f_1) J W_1^*(f_1) J \Omega_{\mathrm{R}_1} \otimes \Omega_{\mathrm{R}_2} \\
&\quad - e^{-\beta\hat\epsilon/2} \varphi_{22} \otimes \Omega_{\mathrm{R}_2} \otimes W_2^*(f_2) J W_2^*(f_2) J \Omega_{\mathrm{R}_2} \big) \\
X_+ &= \varphi_{12} \otimes W^*(f_1) \Omega_{\mathrm{R}_1} \otimes J W^*(f_2) J \Omega_{\mathrm{R}_2} \\
X_- &= \varphi_{21} \otimes J W^*(f_1) J \Omega_{\mathrm{R}_1} \otimes W^*(f_2) \Omega_{\mathrm{R}_2}.
\end{aligned}
\tag{4.43}
$$

Lemma 4.3 shows that

$$\left\langle \psi_0, B U^* \Pi_j U A \Omega_{\beta,\vec\lambda,0} \right\rangle = \langle \psi_0, B X_j \rangle \left\langle X_j, A \Omega_{\beta,\vec\lambda,V} \right\rangle. \tag{4.44}$$

By Araki's perturbation theory of KMS states ([4], Theorem 5.4.4), the equilibrium states with $V = 0$ and $V \neq 0$ satisfy

$$\|\Omega_{\beta,\vec\lambda,V} - \Omega_{\beta,\vec\lambda,0}\| \leq e^{\beta V/2} - 1 = O(V). \tag{4.45}$$

Thus,

$$\left\langle \psi_0, B U^* \Pi_j U A \Omega_{\beta,\vec\lambda,0} \right\rangle = \langle \psi_0, B X_j \rangle \left\langle X_j, A \Omega_{\beta,\vec\lambda,0} \right\rangle + O(V). \tag{4.46}$$

The first factor on the right side of (4.46) is linked to the initial condition ψ_0, the second one to the equilibrium $\Omega_{\beta,\vec\lambda,0}$.

Lemma 4.4 *The operators D_j defined in (4.43), (4.38) satisfy*

$$X_j = D_j \Omega_{\beta,\vec\lambda,0}. \tag{4.47}$$

Proof of Proposition 4.4. The equilibrium states for the collective and local models are

$$\Omega_{\beta,\vec{\lambda},0} = \frac{1}{\sqrt{1+e^{-\beta\hat{\epsilon}}}} \begin{cases} e^{-\beta\hat{\epsilon}/2}\varphi_{11} \otimes W^*(f_1)JW^*(f_1)J\Omega_{\mathrm{R}} + \varphi_{22} \otimes W^*(f_2)JW^*(f_2)J\Omega_{\mathrm{R}} \\ \qquad \text{and} \\ e^{-\beta\hat{\epsilon}/2}\varphi_{11} \otimes W^*(f_1)JW^*(f_1)J\Omega_{\mathrm{R}_1} \otimes \Omega_{\mathrm{R}_2}+ \\ \qquad +\varphi_{22} \otimes \Omega_{\mathrm{R}_1} \otimes W^*(f_2)JW^*(f_2)J\Omega_{\mathrm{R}_2} \end{cases} \tag{4.48}$$

The relations (4.47), (4.43) and (4.38) are then easily seen to hold. $\square$

Since the operators D_j commute with B, we have

$$\langle \psi_0, BX_j \rangle = \left\langle \psi_0, BD_j\Omega_{\beta,\vec{\lambda},0} \right\rangle = \langle \psi_0, D_j\psi_0 \rangle = \omega_0(D_j). \tag{4.49}$$

Moreover,

$$\left\langle X_j, A\Omega_{\beta,\vec{\lambda},0} \right\rangle = \omega_{\beta,\vec{\lambda},0}(A) \tag{4.50}$$

Combining (4.49) and (4.50) with (4.44) and (4.46), the expansion (4.39) now follows from (4.30). This completes the proof of Theorem 4.2. $\square$

4.2.3   Proofs of Theorems 3.1 and 3.3

Dynamics of populations and proof of Theorem 3.1. Choosing $A = |\varphi_1\rangle\langle\varphi_1| \otimes \mathbb{1}_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{R}}$ in (4.39) yields the population of the level 1, i.e.,

$$\langle |\varphi_1\rangle\langle\varphi_1| \otimes \mathbb{1}_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{R}} \rangle_t = \mathrm{Tr}\rho_{\mathrm{S}}(t)|\varphi_1\rangle\langle\varphi_1| = \langle \varphi_1, \rho_{\mathrm{S}}(t)\varphi_1 \rangle \equiv [\rho_{\mathrm{S}}(t)]_{11}. \tag{4.51}$$

For this choice of A and for both models, we have

$$\omega_{\beta,\vec{\lambda},0}(D_{\pm}^*A) = 0, \quad \omega_{\beta,\vec{\lambda},0}(D_0^*A) = \frac{e^{-\beta\hat{\epsilon}/2}}{1 + e^{-\beta\hat{\epsilon}}} \tag{4.52}$$

and

$$\omega_0(D_0) = e^{\beta\hat{\epsilon}/2}[\rho_{\mathrm{S}}(0)]_{11} - e^{-\beta\hat{\epsilon}/2}[\rho_{\mathrm{S}}(0)]_{22}. \tag{4.53}$$

Furthermore,

$$\omega_0(D_+) = \sqrt{1 + e^{-\beta\hat{\epsilon}}}\ [\rho_{\mathrm{S}}(0)]_{21} \begin{cases} \langle W^*(f_1)W(f_2)\rangle_{\mathrm{R}} & \text{(collective)} \\ \langle W^*(f_1)\rangle_{\mathrm{R}_1} \langle W(f_2)\rangle_{\mathrm{R}_2} & \text{(local)}, \end{cases} \tag{4.54}$$

and

$$\omega_0(D_-) = e^{\beta\hat{\epsilon}/2}\ \overline{\omega_0(D_+)}. \tag{4.55}$$

Combining (4.39) with (4.52)-(4.55) yields (3.6).

Dynamics of decoherence and proof of Theorem 3.3. Choosing $A = |\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{R}}$ in (4.39) yields the off-diagonal dimer density matrix element,

$$\langle |\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{R}} \rangle_t = \mathrm{Tr}\rho_{\mathrm{S}}(t)|\varphi_2\rangle\langle\varphi_1| = \langle \varphi_1, \rho_{\mathrm{S}}(t)\varphi_2 \rangle \equiv [\rho_{\mathrm{S}}(t)]_{12}. \tag{4.56}$$

For this choice of A and for both models, we have

$$\omega_{\beta,\vec{\lambda},0}(D_0^*A) = 0 = \omega_{\beta,\vec{\lambda},0}(D_+^*A) \tag{4.57}$$

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and

$$\omega_{\beta,\vec{\lambda},0}(D_-^* A) = \frac{\mathrm{e}^{-\beta\hat{\epsilon}/2}}{\sqrt{1+\mathrm{e}^{-\beta\hat{\epsilon}}}} \left\{ \begin{array}{ll} \langle W(f_2)W^*(f_1)\rangle_{\mathrm{R}} & \text{(collective)} \\ \langle W^*(f_1)\rangle_{\mathrm{R}_1} \langle W(f_2)\rangle_{\mathrm{R}_2} & \text{(local)}. \end{array} \right. \tag{4.58}$$

Furthermore,

$$\omega_0(D_-) = \mathrm{e}^{\beta\hat{\epsilon}/2}\sqrt{1+\mathrm{e}^{-\beta\hat{\epsilon}}}\ [\rho_{\mathrm{S}}(0)]_{12} \left\{ \begin{array}{ll} \langle W^*(f_2)W(f_1)\rangle_{\mathrm{R}} & \text{(collective)} \\ \langle W(f_1)\rangle_{\mathrm{R}_1} \langle W^*(f_2)\rangle_{\mathrm{R}_2} & \text{(local)}. \end{array} \right. \tag{4.59}$$

Taking into account (4.57)-(4.59), the expression (B.13) for Γ_∞, and expansion (4.39), we obtain (3.15).

Conclusion

We give a theoretical analysis of a (chlorophyll-based) dimer interacting with collective (spatially correlated) and local (spatially uncorrelated) protein-solvent environments, as they appear in photosynthetic bio-complexes. We formulate the problem in the language of a spin-boson system, in which two excited electron energy levels of two light-sensitive molecules (such as chlorophylls or carotenoids) are described by an effective spin $1/2$. Both spin levels (excited electron states of donor and acceptor) interact with a thermal environment, modeled by bosonic degrees of freedom (quantum linear oscillators). In the case of a correlated thermal environment, a single set of bosonic operators, with the characteristic frequencies of the environment, is introduced. In the case of an uncorrelated thermal environment, two sets of bosonic operators are introduced, one for the donor and one for the acceptor. In either situation, we introduce two independent constants of interaction between the donor and the acceptor and the environment(s).

We develop a mathematically rigorous perturbation theory in which the direct matrix element of the donor-acceptor interaction is a small parameter. This perturbation theory is different from the standard Bloch-Redfield theory where the interaction constant between the dimer and the environment(s) is used as a small parameter. Our approach allows us to consider, in a controlled way, the case of strong interaction constants and ambient temperatures. This is important for applications to real bio-systems.

We derive the explicit expressions for the thermal electron transfer rates, and demonstrate the differences with the standard Marcus expression for the electron transfer rates in the so-called high-temperature regime. We analyze the dynamics of decoherence depending on the parameters of the system. In particular, we demonstrate how long-time coherences naturally occurs in the dimer.

The results of the paper are important for a better understanding of the complicated quantum dynamics a chlorophyll-based dimer undergoes in photosynthetic complexes, for a wide region of parameters and under controlled approximations. Experiments could be used to verify our theoretical predictions.

Acknowledgments

A   The level shift operators

Let χ_0 and $\chi_\pm$ be the orthogonal projections onto the eigenspaces of

$$\widetilde{L}_0 = L_{\mathrm{S}}^{\mathrm{ren}} + L_{\mathrm{R}} \quad \text{or} \quad \widetilde{L}_0 = L_{\mathrm{S}}^{\mathrm{ren}} + L_{\mathrm{R}_1} + L_{\mathrm{R}_2} \tag{A.1}$$

associated to the eigenvalues zero and $\pm\hat{\epsilon}$, where

$$\hat{\epsilon} = \epsilon - \frac{\alpha_1 - \alpha_2}{2}. \tag{A.2}$$

(See also Proposition 4.1.) Explicitly, $\chi_0 = |\varphi_{11}\rangle\langle\varphi_{11}| \otimes P_{\mathrm{R}} + |\varphi_{22}\rangle\langle\varphi_{22}| \otimes P_{\mathrm{R}}$ and $\chi_+ = |\varphi_{12}\rangle\langle\varphi_{12}| \otimes P_{\mathrm{R}}$, $\chi_- = |\varphi_{21}\rangle\langle\varphi_{21}| \otimes P_{\mathrm{R}}$, where we recall that P_{R} is given in (4.35). To each unperturbed eigenvalue of $\widetilde{L}_0$, we associate a level shift operator. The one associated to the eigenvalue zero is (the 2×2 matrix)

$$\Lambda_0 = \chi_0 \widetilde{I}(\widetilde{L}_0 + \mathrm{i}0_+)^{-1}\chi_0^\perp \widetilde{I}\chi_0, \tag{A.3}$$

where $\widetilde{I}$ is the interaction operator, $\widetilde{I}_{\mathrm{col}}$ or $\widetilde{I}_{\mathrm{loc}}$, see (4.19), (4.22). The level shift operators associated to the eigenvalues $\pm\hat{\epsilon}$ are both one-dimensional,

$$\Lambda_+ = \chi_+ \widetilde{I}(\widetilde{L}_0 - \hat{\epsilon} + \mathrm{i}0_+)^{-1}\chi_+^\perp \widetilde{I}\chi_+ \quad \text{and} \quad \Lambda_- = \chi_- \widetilde{I}(\widetilde{L}_0 + \hat{\epsilon} + \mathrm{i}0_+)^{-1}\chi_-^\perp \widetilde{I}\chi_- . \tag{A.4}$$

Proposition 1.1 (1) *Consider the model with the collective environment and set*

$$x(\hat{\epsilon}) = -\frac{\mathrm{i}}{2}\mathrm{Re} \int_0^\infty \mathrm{e}^{-\mathrm{i}\hat{\epsilon}t} \mathrm{e}^{\frac{\mathrm{i}(\lambda_1 - \lambda_2)^2}{\pi}Q_1(t)} \mathrm{e}^{-\frac{(\lambda_1 - \lambda_2)^2}{\pi}Q_2(t)} \mathrm{d}t, \tag{A.5}$$

where $Q_1(t), Q_2(t)$ are given in (2.26). In the basis $\{\varphi_{11}, \varphi_{22}\}$, we have

$$\Lambda_0 = x(\hat{\epsilon}) \begin{pmatrix} 1 & -\mathrm{e}^{-\beta\hat{\epsilon}/2} \\ -\mathrm{e}^{-\beta\hat{\epsilon}/2} & \mathrm{e}^{-\beta\hat{\epsilon}} \end{pmatrix}. \tag{A.6}$$

The eigenvalues of $V^2\Lambda_0$ are 0 and $\mathrm{i}\gamma_{\mathrm{col}}$, where γ_{col} is given in (2.25). Moreover, the one-dimensional level shift operators $\Lambda_\pm$ have the expressions

$$V^2\Lambda_+ = \big(x_{\mathrm{LS}} + \tfrac{\mathrm{i}}{2}\gamma_{\mathrm{col}}\big)|\varphi_{12}\rangle\langle\varphi_{12}| \otimes P_{\mathrm{R}} \quad \text{and} \quad V^2\Lambda_- = \big(-x_{\mathrm{LS}} + \tfrac{\mathrm{i}}{2}\gamma_{\mathrm{col}}\big)|\varphi_{21}\rangle\langle\varphi_{21}| \otimes P_{\mathrm{R}}.$$

(2) *Consider the model with the two local reservoirs. The level shift operator Λ_0 has the form (A.6), where now*

$$x(\hat{\epsilon}) = -\frac{\mathrm{i}}{2}\mathrm{Re} \int_0^\infty \mathrm{e}^{-\mathrm{i}\hat{\epsilon}t} \mathrm{e}^{-\frac{\lambda_1^2}{\pi}\big[Q_2^{(1)}(t) - \mathrm{i}Q_1^{(1)}(t)\big]} \mathrm{e}^{-\frac{\lambda_2^2}{\pi}\big[Q_2^{(2)}(t) - \mathrm{i}Q_1^{(2)}(t)\big]} \mathrm{d}t \tag{A.7}$$

and $Q_1^{(j)}, Q_2^{(j)}$ are given in (2.27). The eigenvalues of $V^2\Lambda_0$ are 0 and $\mathrm{i}\gamma_{\mathrm{loc}}$, where γ_{loc} is given in (2.25). Moreover, the one-dimensional level shift operators $\Lambda_\pm$ have the expression

$$V^2\Lambda_+ = \big(x_{\mathrm{LS}} + \tfrac{\mathrm{i}}{2}\gamma_{\mathrm{loc}}\big)|\varphi_{12}\rangle\langle\varphi_{12}| \otimes P_{\mathrm{R}} \quad \text{and} \quad V^2\Lambda_- = \big(-x_{\mathrm{LS}} + \tfrac{\mathrm{i}}{2}\gamma_{\mathrm{loc}}\big)|\varphi_{21}\rangle\langle\varphi_{21}| \otimes P_{\mathrm{R}}.$$

Proof of Proposition 1.1. **(1)** In the case of a single reservoir, the calculation of the level shift operator Λ_0, (A.6) is an easy transcription of that performed in Proposition 3.5 of [14], where the case $\lambda_1 = -\lambda_2$ was considered. We do not present the details.

(2) Once we have the form (A.6), it is readily seen that the vector $\Psi = \varphi_{11} + e^{\beta\hat{\epsilon}/2}\varphi_{22}$ is in the kernel of Λ_0. Therefore, the eigenvalues of Λ_0 are 0 and $\text{Tr}\Lambda_0 = (1 + e^{-\beta\hat{\epsilon}})x(\hat{\epsilon})$. The relation $e^{-\beta\hat{\epsilon}}x(\hat{\epsilon}) = x(-\hat{\epsilon})$ (see (A.17)) together with (A.7) gives $\text{spec}V^2\Lambda_0 = \{0, i\gamma_{\text{loc}}\}$.

Our task now is to show (A.6). Let

$$L_{\vec{R}} = L_{R_1} + L_{R_2}$$

and write W_1 instead of $W_1(f_1) \otimes \mathbb{1}$ and W_2 for $\mathbb{1} \otimes W_2(f_2)$, where the f_j are given in (4.20). Then

$$
\begin{aligned}
4\Lambda_0\varphi_{11} = {} & \varphi_{11}\langle W_1 W_2^*(L_{\vec{R}} - \hat{\epsilon} + i0^+)^{-1}W_1^* W_2\rangle \\
& + \varphi_{11}\langle JW_1 W_2^* J(L_{\vec{R}} + \hat{\epsilon} + i0^+)^{-1}JW_1^* W_2 J\rangle \\
& - \varphi_{22}\langle JW_1^* W_2 J(L_{\vec{R}} - \hat{\epsilon} + i0^+)^{-1}W_1^* W_2\rangle \\
& - \varphi_{22}\langle W_1^* W_2(L_{\vec{R}} + \hat{\epsilon} + i0^+)^{-1}JW_1^* W_2 J\rangle.
\end{aligned}
\tag{A.8}
$$

If we want to stress the dependence of Λ_0 on $\hat{\epsilon}$ and λ_1, λ_2, we wirte $\Lambda_0(\hat{\epsilon}, \lambda_1, \lambda_2)$. Then (A.8) gives

$$\Lambda_0(\hat{\epsilon}, \lambda_1, \lambda_2)\varphi_{11} = x(\hat{\epsilon}, \lambda_1, \lambda_2)\varphi_{11} + z(\hat{\epsilon}, \lambda_1, \lambda_2)\varphi_{22} \tag{A.9}$$

with

$$
\begin{aligned}
x(\hat{\epsilon}, \lambda_1, \lambda_2) = {} & \tfrac{i}{2}\text{Im}\langle W_1 W_2^*(L_{\vec{R}} - \hat{\epsilon} + i0^+)^{-1}W_1^* W_2\rangle, \\
z(\hat{\epsilon}, \lambda_1, \lambda_2) = {} & -\tfrac{i}{2}\text{Im}\langle W_1^* W_2(L_{\vec{R}} + \hat{\epsilon} + i0^+)^{-1}JW_1^* W_2 J\rangle.
\end{aligned}
\tag{A.10}
$$

We use the relation $(L_{\vec{R}} - \hat{\epsilon} + ir)^{-1} = -i\int_0^\infty e^{it(L_{\vec{R}} - \hat{\epsilon} + ir)}dt$ (for $r > 0$) to obtain

$$x(\hat{\epsilon}, \lambda_1, \lambda_2) = -\tfrac{i}{2}\lim_{r\to 0_+}\text{Re}\int_0^\infty e^{i(-\hat{\epsilon}+ir)t}\langle W_1(f_1)W_1(-e^{it\omega}f_1)\rangle\,\langle W_2(-f_2)W_2(e^{it\omega}f_2)\rangle dt. \tag{A.11}$$

With the canonical commutation relations $W(f)W(g) = e^{-\frac{i}{2}\text{Im}\langle f,g\rangle}W(f + g)$ and the thermal average $\langle W(f)\rangle = \exp -\frac{1}{4}\langle f, \coth(\beta\omega/2)f\rangle$ we arrive at

$$\langle W(f)W(-e^{it\omega}f)\rangle = e^{\frac{i}{2}\langle f,\sin(\omega t)f\rangle}e^{-\frac{1}{2}\langle f,(1-\cos(\omega t))\coth(\beta\omega/2)f\rangle}.$$

Then, remembering the definition (4.20) of f_j, we arrive at

$$
\begin{aligned}
& x(\hat{\epsilon}, \lambda_1, \lambda_2) \\
& = -\tfrac{i}{2}\lim_{r\to 0_+}\text{Re}\int_0^\infty e^{i(-\hat{\epsilon}+ir)t}e^{\frac{i}{2}\lambda_1^2\langle g_1,\frac{\sin\omega t}{\omega^2}g_1\rangle - \frac{1}{2}\lambda_1^2\langle g_1,\frac{1-\cos\omega t}{\omega^2}\coth(\beta\omega/2)g_1\rangle} \\
& \qquad \times e^{\frac{i}{2}\lambda_2^2\langle g_2,\frac{\sin\omega t}{\omega^2}g_2\rangle - \frac{1}{2}\lambda_2^2\langle g_2,\frac{1-\cos\omega t}{\omega^2}\coth(\beta\omega/2)g_2\rangle}dt,
\end{aligned}
\tag{A.12}
$$

which is the expression for $x(\hat{\epsilon})$ given in (A.7). Note that x is invariant under a sign change of either λ_1 or λ_2.

Next, we find an expression for $z(\hat{\epsilon}, \lambda_1, \lambda_2)$. Starting with the definition (A.10) and replacing the resolvent by an integral over the propagator, as above, yields the expression

$$z(\hat{\epsilon}, \lambda_1, \lambda_2) = \tfrac{1}{2} \int_0^\infty \cos(\hat{\epsilon}t) \; \alpha(f_1, -\mathrm{e}^{\mathrm{i}t\omega} f_1)\alpha(f_2, -\mathrm{e}^{\mathrm{i}t\omega} f_2)\mathrm{d}t, \tag{A.13}$$

where

$$\alpha(f, g) = \mathrm{e}^{\frac{1}{4}\{\langle f, \mathrm{e}^{-\beta w/2} g\rangle - \langle g, \mathrm{e}^{\beta w/2} f\rangle\}} \mathrm{e}^{-\frac{1}{4}\{\langle f, Cf\rangle + \langle g, Cg\rangle - \langle g, C\mathrm{e}^{\beta w/2} f\rangle - \langle f, C\mathrm{e}^{-\beta w/2} g\rangle\}}, \tag{A.14}$$

with $C = \coth(\beta\omega/2)$. Relation (A.13) shows that z is invariant under changing signs of either of $\hat{\epsilon}$, λ_1 and λ_2. Note also that z is real.

The symmetry

$$(\sigma_x \otimes \sigma_x) \, \Lambda_0(\hat{\epsilon}, \lambda_1, \lambda_2) \, (\sigma_x \otimes \sigma_x) = \Lambda_0(-\hat{\epsilon}, -\lambda_1, -\lambda_2)$$

together with (A.9) and the fact that $(\sigma_x \otimes \sigma_x)\varphi_{11} = \varphi_{22}$ yields

$$\Lambda_0(\hat{\epsilon}, \lambda_1, \lambda_2)\varphi_{22} = z(-\hat{\epsilon}, -\lambda_1, -\lambda_2)\varphi_{11} + x(-\hat{\epsilon}, -\lambda_1, -\lambda_2)\varphi_{22}. \tag{A.15}$$

We show below that

$$z(\hat{\epsilon}, \lambda_1, \lambda_2) = -\mathrm{e}^{-\beta\hat{\epsilon}/2} x(\hat{\epsilon}, \lambda_1, \lambda_2). \tag{A.16}$$

Together with the invariance of z under flipping the sign of $\hat{\epsilon}$, this gives

$$x(-\hat{\epsilon}) = \mathrm{e}^{-\beta\hat{\epsilon}} x(\hat{\epsilon}). \tag{A.17}$$

This shows the form (A.6), modulo showing relation (A.16). We prove (A.16) now. Set $\chi = W_1^*\Omega_1 \otimes W_2\Omega_2$ and consider, for $r > 0$,

$$\mathrm{Im} \left\langle \chi, (L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}r)^{-1}\chi \right\rangle = -\left\langle \chi, \frac{r}{(L_{\vec{R}} - \hat{\epsilon})^2 + r^2}\chi \right\rangle$$

$$= -\left\langle \chi, \frac{r}{(L_{\vec{R}} - \hat{\epsilon})^2 + r^2} \left[\mathrm{e}^{-\beta(L_{\vec{R}} - \hat{\epsilon})/2} + 1 - \mathrm{e}^{-\beta(L_{\vec{R}} - \hat{\epsilon})/2}\right]\chi \right\rangle. \tag{A.18}$$

Since

$$\mathrm{e}^{-\beta L_{\vec{R}}/2}\chi = J \cdot J\mathrm{e}^{-\beta L_{\vec{R}}/2}(W_1^*\Omega_1 \otimes W_2\Omega_2) = J(W_1\Omega_1 \otimes W_2^*\Omega_2) \tag{A.19}$$

is well defined, we can separate the terms in (A.18). We have used in the last step in (A.19) that $J\mathrm{e}^{-\beta L_{\vec{R}}/2}(A_1\Omega_1 \otimes A_2\Omega) = A_1^*\Omega_1 \otimes A_2^*\Omega_2$ (by the properties of the modular conjugation J and the modular operator $\Delta = \mathrm{e}^{-\beta L_{\vec{R}}}$). Then, by (A.19),

$$-\left\langle \chi, \frac{r}{(L_{\vec{R}} - \hat{\epsilon})^2 + r^2}\mathrm{e}^{-\beta(L_{\vec{R}} - \hat{\epsilon})/2}\chi \right\rangle = \mathrm{e}^{\beta\hat{\epsilon}/2}\mathrm{Im} \left\langle \chi, (L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}r)^{-1}\mathrm{e}^{-\beta L_{\vec{R}}/2}\chi \right\rangle$$

$$= \mathrm{e}^{\beta\hat{\epsilon}/2}\mathrm{Im}\langle W_1 W_2^*(L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}r)^{-1}JW_1W_2^*\rangle. \tag{A.20}$$

Next, by the functional calculus,

$$\left\langle \chi, \frac{r}{(L_{\vec{R}} - \hat{\epsilon})^2 + r^2}[1 - \mathrm{e}^{-\beta(L_{\vec{R}} - \hat{\epsilon})/2}]\chi \right\rangle = \int_{\mathbb{R}} \frac{r\,(x - \hat{\epsilon})}{(x - \hat{\epsilon})^2 + r^2}\frac{1 - \mathrm{e}^{-\beta(x - \hat{\epsilon})/2}}{(x - \hat{\epsilon})}\mathrm{d}\mu_\chi(x), \tag{A.21}$$

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where $d\mu_\chi(x)$ is the spectral measure of $L_{\vec{R}}$ in the state χ. One readily sees that the integrand satisfies the bound

$$\left| \frac{r(x - \hat{\epsilon})}{(x - \hat{\epsilon})^2 + r^2} \frac{1 - e^{-\beta(x-\hat{\epsilon})/2}}{(x - \hat{\epsilon})} \right| \le C(1 + e^{-\beta(x-\hat{\epsilon})/2}),$$

independently of r. The right side is integrable w.r.t. $d\mu_\chi(x)$ since χ is in the domain of definition of $e^{-\beta L_{\vec{R}}/2}$. Then, since the integrand in (A.21) converges to zero as $r \to 0$, for all $x \in \mathbb{R}\backslash\{\hat{\epsilon}\}$, and since $\{\hat{\epsilon}\}$ has measure zero w.r.t. $d\mu_\chi(x)$ (as $\hat{\epsilon} \ne 0$ is not an eigenvalue of $L_{\vec{R}}$), we can apply the Dominated Convergence Theorem to conclude that

$$\lim_{r \to 0} \left\langle \chi, \frac{r}{(L_{\vec{R}} - \hat{\epsilon})^2 + r^2}[1 - e^{-\beta(L_{\vec{R}} - \hat{\epsilon})/2}]\chi \right\rangle = 0. \tag{A.22}$$

It follows from (A.18), (A.20) and (A.22) that

$$\mathrm{Im}\langle W_1 W_2^*(L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}0_+)^{-1}W_1^* W_2\rangle = e^{\beta\hat{\epsilon}/2}\mathrm{Im}\langle W_1 W_2^*(L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}0_+)^{-1}JW_1 W_2^*\rangle. \tag{A.23}$$

Relation (A.12) shows that $x(\hat{\epsilon})$ is invariant under a change of the sign of λ_1 and λ_2 (independently), so interchanging $W_1 \leftrightarrow W_1^*$ and $W_2 \leftrightarrow W_2^*$ in the expression (A.10) for $x(\hat{\epsilon})$ does not change the value of the expression. Thus we have

$$x(\hat{\epsilon}) = \tfrac{\mathrm{i}}{2}\mathrm{Im}\langle W_1^* W_2(L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}0^+)^{-1}W_1 W_2^*\rangle = \tfrac{\mathrm{i}}{2}e^{\beta\hat{\epsilon}/2}\mathrm{Im}\langle W_1^* W_2(L_{\vec{R}} - \hat{\epsilon} + \mathrm{i}0_+)^{-1}JW_1^* W_2\rangle,$$

where we have used (A.23) in the last step (with $\lambda_{1,2}$ replaced by $-\lambda_{1,2}$). The definition (A.10) for $z(\hat{\epsilon})$ shows that the expression on the right side is $-e^{\beta\hat{\epsilon}/2}z(-\hat{\epsilon})$. Therefore we have proven the relation $z(-\hat{\epsilon}) = -e^{-\beta\hat{\epsilon}/2}x(\hat{\epsilon})$, which yields (A.16) since $z(-\hat{\epsilon}) = z(\hat{\epsilon})$. This completes the proof of (A.6).

Finally, the forms of $\Lambda_\pm$ given at the end of the proposition are checked directly by a simple calculation. This completes the proof of Proposition 1.1. $\qquad\square$

B   System for $V = 0$, factor $e^{-\Gamma_\infty}$

B.1   Equilibrium for $V = 0$

In the setting of the collective reservoir, let

$$u = e^{\mathrm{i}P_1 \otimes \phi(f_1) + \mathrm{i}P_2 \otimes \phi(f_2)} = P_1 \otimes W(f_1) + P_2 \otimes W(f_2), \tag{B.1}$$

where $f_j = \mathrm{i}\lambda_j g/\omega$. A direct calculation shows that

$$u H_{\mathrm{col}} u^* = \tfrac{1}{2}\begin{pmatrix} \epsilon - 2\lambda_1^2\nu/\pi & 0 \\ 0 & -\epsilon - 2\lambda_2^2\nu/\pi \end{pmatrix} + H_{\mathrm{R}} + \tfrac{V}{2}\left(\sigma_+ \otimes W\big((\lambda_1 - \lambda_2)g/(\mathrm{i}\omega)\big) + \mathrm{h.c.}\right), \tag{B.2}$$

where ν is given in (2.26) and σ_+ is the raising operator. To calculate the equilibrium state with $V = 0$, we note that

$$e^{-\beta H_{\mathrm{col}}(V=0)} = u^* e^{-\beta u H_{\mathrm{col}}(V=0)u^*} u = u^*\big(e^{-\frac{\beta}{2}(\epsilon - 2\lambda_1^2\nu/\pi)}P_1 + e^{-\frac{\beta}{2}(-\epsilon - 2\lambda_2^2\nu/\pi)}P_2\big) \otimes e^{-\beta H_{\mathrm{R}}}\, u. \tag{B.3}$$

Now (3.2) follows readily from (B.3) and (B.1).

In the situation of the local reservoirs model, set $u = e^{\mathrm{i}P_1 \otimes \phi_1(f_1) + \mathrm{i}P_2 \otimes \phi_2(f_2)}$, where $f_j = \mathrm{i}\lambda_j g_j/\omega$, and proceed as above to show (3.5).

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B.2 Decoherence for $V = 0$, proof of Proposition 3.2

Using the same notation as in Section B.1 we have

$$[\rho_S(t)]_{12} = \text{Tr} \left(e^{-ituH_{\text{col}}u^*} u(\rho_S(0) \otimes \rho_R) u^* e^{ituH_{\text{col}}u^*} u(|\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_R) u^* \right). \tag{B.4}$$

Using the form (B.2) and that $u(|\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_R)u^* = |\varphi_2\rangle\langle\varphi_1| \otimes W(f_2)W^*(f_1)$ (and the suitable expressions for the local reservoirs model), we arrive at the following expression, for both the local and collective reservoirs models,

$$[\rho_S(t)]_{12} = \mathcal{D}(t) \, e^{-it\hat{\epsilon}}[\rho_S(0)]_{12}, \tag{B.5}$$

where

$$\mathcal{D}(t) = \begin{cases} \langle W^*(f_2)W(f_2(t))W^*(f_1(t))W(f_1)\rangle_R & \text{(collective)} \\ \langle W^*(f_2)W(f_2(t))\rangle_R \, \langle W^*(f_1(t))W(f_1)\rangle_R & \text{(local)} \end{cases} \tag{B.6}$$

Here, $W(f(t)) = e^{itH_R}W(f)e^{-itH_R} = W(e^{it\omega}f)$. Then, using the canonical commutation relations $W(f)W(g) = e^{-\frac{i}{2}\text{Im}\langle f,g\rangle}W(f+g)$ and the thermal average $\langle W(f)\rangle_R = e^{-\frac{1}{4}\langle f,\coth(\beta\omega/2)f\rangle}$, (3.10) follows directly from (B.6) and the definitions of the functions Q (see (2.26), (2.27)).

We now show Proposition 3.2. The reservoir alone has the property of 'return to equilibrium', which can be expressed as follows.

Lemma 2.1 *Let A, B and C be observables of the reservoir and set $B(t) = e^{itL_R}Be^{-itL_R}$. Then we have*

$$\lim_{t\to\infty} \langle AB(t)C\rangle_R = \langle AC\rangle_R \, \langle B\rangle_R. \tag{B.7}$$

Proof of Lemma 2.1. For any $\epsilon > 0$ there exists a C'_ϵ which commutes with all observables and which satisfies

$$\|C\Omega_R - C'_\epsilon\Omega_R\| \le \epsilon. \tag{B.8}$$

This is simply the separability of Ω_R. Therefore,

$$\langle AB(t)C\rangle_R = \langle AB(t)C'_\epsilon\rangle_R + R_1(\epsilon), \tag{B.9}$$

where $|R_1(\epsilon)| \le \epsilon\|A\|\,\|B\|$. Next, since C'_ϵ commutes with $B(t)$ and since $e^{-itL_R}\Omega_R = \Omega_R$, we have

$$\langle AB(t)C'_\epsilon\rangle_R = \langle AC'_\epsilon e^{itL_R}B\rangle_R = \langle AC'_\epsilon\rangle_R \, \langle B\rangle_R + R_2(\epsilon, t), \tag{B.10}$$

with

$$\lim_{t\to 0} R_2(\epsilon, t) = 0, \quad \forall \epsilon > 0. \tag{B.11}$$

Relation (B.11) follows from the fact that $e^{itL_R} \to |\Omega_R\rangle\langle\Omega_R|$ in the weak sense as $t \to \infty$ (which in turn is implied by the fact that L_R has absolutely continuous spectrum except for a simple eigenvalue at zero, with eigenvector Ω_R.) Also, the term $\langle AC'_\epsilon\rangle_R$ in (B.10) equals $\langle AC\rangle + R_3(\epsilon)$, with $|R_3(\epsilon)| \le \epsilon\|A\|$, by (B.8). We finally obtain

$$\langle AB(t)C\rangle_R - \langle AC\rangle_R \, \langle B\rangle_R = R_4(\epsilon) + R_2(\epsilon, t), \tag{B.12}$$

with $|R_4(t)| \le 2\epsilon \|A\| \|B\|$ and $R_2(\epsilon, t)$ satisfying (B.11).

Relation (B.12) implies (B.7). □

It follows from Lemma 2.1 that

$$\lim_{t\to\infty} \mathcal{D}(t) = \langle W^*(f_2)W(f_1)\rangle_R \, \langle W(f_2)W^*(f_1)\rangle_R = \mathrm{e}^{-\Gamma_\infty}, \tag{B.13}$$

where Γ_∞ is given in (3.12).

For the model with the local reservoirs, the relations (B.5) and $\lim_{t\to\infty} \mathcal{D}(t) = \mathrm{e}^{-\Gamma_\infty}$ are derived in the same way. This finishes the proof of Proposition (3.2) □

B.3 Explanation of the factor $\mathrm{e}^{-\Gamma_\infty}$ in (3.15).

In the basic resonance expansion (4.30), for $A = |\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_S \otimes \mathbb{1}_R$, all terms on the right side except the one with Π_- are $O(V)$. Thus

$$
\begin{aligned}
[\rho_S(t)]_{12} &= \mathrm{e}^{-\gamma t/2}\mathrm{e}^{-it(\hat\epsilon + x_{LS})} \left\langle UB^*\psi_0, \big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes |\Omega_R\rangle\langle\Omega_R|\big) UA\Omega_{\beta,\vec\lambda,V} \right\rangle \\
&\quad + O(V) + R(t).
\end{aligned}
\tag{B.14}
$$

The projection $|\Omega_R\rangle\langle\Omega_R|$ is the (weak) limit $\lim_{t\to\infty} \mathrm{e}^{itL_R}$ and so the scalar product term on the right side of (B.14) is

$$
\begin{aligned}
&\lim_{t\to\infty} \mathrm{e}^{it\hat\epsilon} \left\langle UB^*\psi_0, \mathrm{e}^{it\widetilde{L}_0}\big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes \mathbb{1}_R\big) UA\Omega_{\beta,\vec\lambda,V} \right\rangle \\
&= \lim_{t\to\infty} \mathrm{e}^{it\hat\epsilon} \left\langle UB^*\psi_0, \mathrm{e}^{it\widetilde{L}_0}\big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes \mathbb{1}_R\big) UA\Omega_{\beta,\vec\lambda,0} \right\rangle + O(V).
\end{aligned}
\tag{B.15}
$$

Here, $\widetilde{L}_0$ is given in (A.1) and we have made use of the fact $L_S^{\mathrm{ren}}\varphi_{21} = -\hat\epsilon\varphi_{21}$ and relation (4.45). One readily sees that

$$
\begin{aligned}
\big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes \mathbb{1}_R\big) UA\Omega_{\beta,\vec\lambda,0} &= U\big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes \mathbb{1}_R\big) A\Omega_{\beta,\vec\lambda,0} \\
&= U\big(|\varphi_2\rangle\langle\varphi_1| \otimes |\varphi_1\rangle\langle\varphi_1| \otimes \mathbb{1}_R\big)\Omega_{\beta,\vec\lambda,0} \\
&= UA\Omega_{\beta,\vec\lambda,0}.
\end{aligned}
\tag{B.16}
$$

The last equality follows from the explicit form (4.48) of $\Omega_{\beta,\vec\lambda,0}$. Using (B.16) in (B.15) shows that

$$
\begin{aligned}
\left\langle UB^*\psi_0, \mathrm{e}^{it\widetilde{L}_0}\big(|\varphi_{21}\rangle\langle\varphi_{21}| \otimes \mathbb{1}_R\big) UA\Omega_{\beta,\vec\lambda,0} \right\rangle &= \left\langle \psi_0, B\mathrm{e}^{itL|_{V=0}}A\Omega_{\beta,\vec\lambda,0} \right\rangle \\
&= \left\langle \psi_0, B\mathrm{e}^{itL|_{V=0}}A\mathrm{e}^{-itL|_{V=0}}\Omega_{\beta,\vec\lambda,0} \right\rangle = \left\langle \psi_0, \mathrm{e}^{itL|_{V=0}}A\mathrm{e}^{-itL|_{V=0}}B\Omega_{\beta,\vec\lambda,0} \right\rangle \\
&= \left\langle \psi_0, \mathrm{e}^{itL|_{V=0}}A\mathrm{e}^{-itL|_{V=0}}\psi_0 \right\rangle + O(V) \\
&= \mathcal{D}(t)\mathrm{e}^{-it\hat\epsilon}[\rho_S(0)]_{12} + O(V).
\end{aligned}
\tag{B.17}
$$

the last equality is obtained from (B.5), since $\left\langle \psi_0, \mathrm{e}^{itL|_{V=0}}A\mathrm{e}^{-itL|_{V=0}}\psi_0 \right\rangle$ is exactly the $(1,2)$ matrix element of the dimer density matrix at time t, evolving according to the evolution with $V = 0$. We combine (B.17) with (B.15) and (B.14) to reach

$$[\rho_S(t)]_{12} = \mathrm{e}^{-\gamma t/2}\mathrm{e}^{-it(\hat\epsilon + x_{LS})}\Big\{\lim_{t\to\infty}\mathcal{D}(t)\Big\}[\rho_S(0)]_{12} + O(V) + R(t). \tag{B.18}$$

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Upshot. The rigorous derivation the formula (B.18) given above can be put into heuristic words, uncovering the mechanism making $\mathrm{e}^{-\Gamma_\infty} = \lim_{t\to\infty} \mathcal{D}(t)$ appear in (3.15), as follows. The resonance approximation (c.f. (4.30)) consists in replacing the propagator $\mathrm{e}^{\mathrm{i}tL} \sim \sum_j \mathrm{e}^{\mathrm{i}ta_j}\Pi_j + R(t)$, where $a_j \in \mathbb{C}$ are complex resonance energies and Π_j are projections. While the a_j depend on V, the projections Π_j are lowest oder approximations (i.e. $O(V^0)$) and hence independent of V. The observable $A = |\varphi_2\rangle\langle\varphi_1| \otimes \mathbb{1}_\mathrm{S} \otimes \mathbb{1}_\mathrm{R}$ selects a single projection, $\Pi_- = |\varphi_2\rangle\langle\varphi_2| \otimes |\varphi_1\rangle\langle\varphi_1| \otimes P_\mathrm{R}$, in that all other terms are $O(V)$,

$$\mathrm{e}^{\mathrm{i}tL}A \sim \sum_j \mathrm{e}^{\mathrm{i}ta_j}\Pi_j A + R(t) = \mathrm{e}^{\mathrm{i}ta_-}\Pi_- A + O(V) + R(t).$$

Due to the dispersiveness of the reservoir(s), we have $P_\mathrm{R} = \lim_{t\to\infty} \mathrm{e}^{\mathrm{i}tL_\mathrm{R}}$, so that Π_- is the long-time limit of the dynamics with $V=0$, i.e., $\Pi_j \sim \lim_{t\to\infty} \mathrm{e}^{\mathrm{i}tL|_{V=0}}$. Thus,

$$\mathrm{e}^{\mathrm{i}tL}A \sim \mathrm{e}^{\mathrm{i}ta_-} \lim_{t\to\infty} \mathrm{e}^{\mathrm{i}tL|_{V=0}}A + O(V) + R(t).$$

This is the form (B.18), which can be rewritten as (see (B.5))

$$[\rho_\mathrm{S}(t)]_{21} = \mathrm{e}^{-\gamma t/2}\mathrm{e}^{-\mathrm{i}t(\hat{\epsilon}+x_\mathrm{LS})} \lim_{t\to\infty} \mathrm{e}^{\mathrm{i}t\hat{\epsilon}}\big[\rho_\mathrm{S}(t,V=0)\big]_{12} + O(V) + R(t), \tag{B.19}$$

where $\rho_\mathrm{S}(t,V=0)$ is the dimer density matrix at time t, evolving under the dynamics coupled with the reservoir(s) with $V=0$. In (B.19), $\lim_{t\to\infty} \mathrm{e}^{\mathrm{i}t\hat{\epsilon}}\big[\rho_\mathrm{S}(t,V=0)\big]_{12}$ can be considered as a 'shifted initial condition' for the off-diagonal dimer density matrix.

The analogous analysis holds for the populations, e.g. for $[\rho_\mathrm{S}(t)]_{1,1}$. However, since the populations are stationary under the coupled dimer-reservoir(s) evolution with $V=0$, we have $[\rho_\mathrm{S}(t,V=0)]_{11} = [\rho_\mathrm{S}(0)]_{11}$ for all times. Thus the shifted initial condition coincides with the true one and the analogue of the factor $\mathrm{e}^{-\Gamma_\infty}$ is just the factor 1 for the populations.

B.4   Origin of full and partial phase decoherence

We limit our discussion here to the situation of a collective reservoir and symmetric coupling, i.e., $\lambda_1 = -\lambda_2$.

B.4.1   Quantum noise

Consider the dimer coupled to the collective reservoir with $V=0$, and where $\lambda_1 = -\lambda_2 = \lambda$. The Hamiltonian is (c.f. (2.1))

$$H = \frac{\epsilon}{2}\sigma_z + H_R + \lambda\sigma_z \otimes \phi(g). \tag{B.20}$$

One readily verifies that the exact solution for the off-diagonal dimer density matrix element is[4]

$$[\rho_\mathrm{S}(t)]_{12} = \mathrm{e}^{-\mathrm{i}\epsilon t}[\rho_\mathrm{S}(0)]_{12} \operatorname{Tr}_\mathrm{R}\big(\rho_\mathrm{R}\, \mathrm{e}^{-2\mathrm{i}\lambda \int_0^t \phi(\mathrm{e}^{\mathrm{i}\omega s}g)}\big). \tag{B.21}$$

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[4] One way to do this is to pass to the interaction picture, $\widetilde{\rho}(t) = \mathrm{e}^{\mathrm{i}tH_0}\widetilde{\rho}(0)\mathrm{e}^{-\mathrm{i}tH_0}$, where H_0 is (B.20) with $\lambda = 0$, and then write the evolution for $\widetilde{\rho}(t)$ using a time-dependent generator for the propagator.

Let
$$\phi_s = \phi(e^{i\omega s}g) \tag{B.22}$$

and denote
$$\langle\cdot\rangle = \mathrm{Tr}_{\mathrm{R}}(\rho_{\mathrm{R}} \cdot). \tag{B.23}$$

Then
$$\langle e^{-2i\lambda\int_0^t \phi_s ds}\rangle = \sum_{n\geq 0} \frac{(-2i\lambda)^n}{n!} \int_0^t ds_1 \cdots \int_0^t ds_n \, \langle\phi_{s_1}\cdots\phi_{s_n}\rangle. \tag{B.24}$$

The process ϕ_t is (non-commutative) Gaussian. Namely, the n-point correlations functions are expressed solely using two-point correlations according to "Wick's theorem" (c.f. [4] for example),
$$\langle\phi_{s_1}\cdots\phi_{s_{2k}}\rangle = \sum_{\mathrm{pairings}} \langle\phi_{s_{i_1}}\phi_{s_{j_1}}\rangle\cdots\langle\phi_{s_{i_k}}\phi_{s_{j_k}}\rangle, \tag{B.25}$$

and the correlation functions of odd order vanish. Here, the sum in (B.25) is over the
$$(k-1)!! = (k-1)(k-3)\cdots 5\cdot 3\cdot 1 = 2^{-k+1}\frac{(2k-1)!}{(k-1)!} \tag{B.26}$$

pairings of the indices. Now
$$\int_0^t ds_1 \cdots \int_0^t ds_{2k} \, \langle\phi_{s_1}\cdots\phi_{s_{2k}}\rangle = \sum_{\mathrm{pairings}} \left(\alpha_Q(t)\right)^k = 2^{-k+1}\frac{(2k-1)!}{(k-1)!}\left(\alpha_Q(t)\right)^k, \tag{B.27}$$

where
$$\alpha_Q(t) = \int_0^t ds \int_0^t dr \, \langle\phi_s\phi_r\rangle. \tag{B.28}$$

We use (B.27) in (B.24) and get
$$\langle e^{-2i\lambda\int_0^t \phi_s ds}\rangle = \sum_{k\geq 0} \frac{(-2i\lambda)^{2k}}{(2k)!} 2^{-k+1}\frac{(2k-1)!}{(k-1)!}\left(\alpha_Q(t)\right)^k = e^{-2\lambda^2\alpha_Q(t)}. \tag{B.29}$$

A direct calculation shows that
$$\alpha_Q(t) = \frac{2}{\pi}Q_2(t), \tag{B.30}$$

where $Q_2(t)$ is given in (2.26). Relation (B.21) is thus the same as (2.20) and $\mathcal{D}(t)$ is expressed via α_Q, the double integral over the correlation function, as
$$\mathcal{D}(t) = e^{-2\lambda^2\alpha_Q(t)} = e^{-\frac{4}{\pi}Q_2(t)}. \tag{B.31}$$

B.4.2   Comparison with classical noise

Instead of considering a quantum mechanical noise as in the previous section, one may introduce a time-dependent Hamiltonian (including an "external noise") as
$$H(t) = \frac{\epsilon}{2}\sigma_z + \lambda\sigma_z\xi_t, \tag{B.32}$$

where ξ_t is a commutative stochastic process. The exact solution for the off-diagonal density matrix element for each realization of the noise ξ_t is $[\rho_S(t)]_{12} = e^{-i\epsilon t}[\rho_S(0)]_{12}\,e^{-2i\lambda\int_0^t \xi_s ds}$ and taking the average $\langle\cdot\rangle$ over the noise gives

$$[\rho_S(t)]_{12} = e^{-i\epsilon t}[\rho_S(0)]_{12}\,\langle e^{-2i\lambda\int_0^t \xi_s ds}\rangle. \tag{B.33}$$

We have again

$$\langle e^{-2i\lambda\int_0^t \xi_s ds}\rangle = \sum_{n\geq 0}\frac{(-2i\lambda)^n}{n!}\int_0^t ds_1 \cdots \int_0^t ds_n\,\langle\xi_{s_1}\cdots\xi_{s_n}\rangle. \tag{B.34}$$

and if ξ_t is a Gaussian process, then by the Gaussian Moment Theorem (Wick's Theorem), just as in the quantum case,

$$\langle\xi_{s_1}\cdots\xi_{s_{2k}}\rangle = \sum_{\text{pairings}}\langle\xi_{s_{i_1}}\xi_{s_{j_1}}\rangle\cdots\langle\xi_{s_{i_k}}\xi_{s_{j_k}}\rangle, \tag{B.35}$$

and the correlation functions of odd order vanish. We then get in the same way as for the quantum case

$$\langle e^{-2i\lambda\int_0^t \xi_s ds}\rangle = e^{-2\lambda^2\alpha_C(t)}, \quad \text{where} \quad \alpha_C(t) = \int_0^t ds \int_0^t dr\,\langle\xi_s\xi_r\rangle. \tag{B.36}$$

Comparing (B.29) and (B.36) shows that decoherence in the classical and the quantum noise case is *exactly the same* if the noises have the same characteristics, i.e., if ξ_t is Gaussian with zero average and two-point function $\langle\xi_s\xi_r\rangle = \langle\phi_s\phi_r\rangle$.

B.4.3 Full versus partial decoherence

For either the classical or quantum noise, consider the correlation function

$$C(t,s) = \frac{1}{2}\big(\langle\phi_t\phi_s\rangle + \langle\phi_s\phi_t\rangle\big) \quad \text{or} \quad C(t,s) = \frac{1}{2}\big(\langle\xi_t\xi_s\rangle + \langle\xi_s\xi_t\rangle\big). \tag{B.37}$$

For stationary processes, $C(t,s) = C(t-s)$ and so $C(t,s) = C(|t-s|)$. Then

$$\alpha(t) = \int_0^t ds \int_0^t dr\,C(|s-r|) = 2\int_0^t ds \int_0^s d\tau\,C(\tau). \tag{B.38}$$

We have

$$\text{Full decoherence} \quad \Longleftrightarrow \quad \lim_{t\to\infty}\alpha(t) = \infty. \tag{B.39}$$

Only the decay asymptotics of the correlation function plays a role to determine if $\alpha(t) \to \infty$ or not. Assume

$$C(\tau) \sim \tau^{-\delta}, \quad \text{for some } \delta \geq 0 \text{ and for } \tau \text{ large.} \tag{B.40}$$

Then $\alpha(t) \sim t^{2-\delta}$ for large t, so we have full decoherence exactly if $\delta \leq 2$ (for $\delta = 2$, we have $\alpha(t) \sim \ln t$). This holds equally well for quantum and classical noises.

Discussion for the quantum thermal noise. One has

$$C(\tau) = \frac{1}{2} \operatorname{Re} \int_0^\infty e^{i\omega\tau} J(\omega) \coth(\beta\omega/2) d\omega, \tag{B.41}$$

where $J(\omega)$ is the spectral density of noise (3.1). To find the decay of the correlation function, write

$$(i\tau)^n C(\tau) = \frac{1}{2} \operatorname{Re} \int_0^\infty \left(\frac{d^n}{d\omega^n} e^{i\omega\tau}\right) J(\omega) \coth(\beta\omega/2) d\omega. \tag{B.42}$$

Assume the form

$$J(\omega) \sim \omega^\gamma \quad \text{for } \omega \text{ small} \tag{B.43}$$

and that $J(\omega)$ decays at least as ω^{-n} for large ω. By integrating (B.42) by parts to transfer the action of the ω-derivatives onto the function $J(\omega) \coth(\beta\omega/2)$, one easily finds that

$$\limsup_{\tau \to \infty} |\tau^n C(\tau)| < \infty \iff \gamma > n. \tag{B.44}$$

According to the discussion after (B.40), the critical value for full decoherence is $n = 2$, so if $J(\omega)$ vanishes more quickly than ω^2 for small ω, then we do not have full decoherence. In this way, the decay speed of correlations is governed by the low frequency behavior of the spectral density of noise and therefore, this behavior determines whether we have or do not have full decoherence. We can sum this up:

The low frequency modes of the reservoir are responsible for full decoherence. We have full decoherence if and only if the low frequency modes are well coupled to the dimer. More precisely, we have full decoherence if and only if $J(\omega) \sim \omega^\gamma$ with $\gamma \leq 2$ as $\omega \sim 0$.

[Note: In [29], (p. 577), it is mentioned that the effect of non-full decoherence is due to "...the suppressed influence of low-frequency fluctuations...", which coincides with the picture we uncover here.]

C Mathematical regularity requirements

We specify the precise regularity requirements which lead to (2.8) and (2.9). The spectral function of the reservoir is linked to the form factor by $J(\omega) = \frac{\pi}{2}\omega^2 \int_{S^2} |g(\omega, \Sigma)| d\Sigma$ and the form (2.8) corresponds to

$$g(k) = \frac{|k|^p}{(1 + |k|)^\sigma} \widetilde{g}(k), \tag{C.1}$$

where $\widetilde{g}(k)$ is a (real valued) function which satisfies $\sup_{k \in \mathbb{R}^3} |\partial_\omega^j \widetilde{g}(\omega, \Sigma)| < \infty$ for $j = 0, \dots, 4$. Here, $k = (\omega, \Sigma) \in \mathbb{R}_+ \times S^2$ is the spherical representation of vectors k. There are two origins of the infrared regularity needed here. One is the application of a 'polaron transformation' (c.f. Proposition 4.1), which is indispensable in order to deal with arbitrary values of λ_1 and λ_2 and which requires only the milder regularity $p > -1/2$. The other origin is that we use a 'dynamical resonance theory' developed in [13], which gives a proof of (4.30) under the assumptions that

$$uh, \; \partial_u^j h \in L^2(\mathbb{R} \times S^2, \mathrm{d}u \times \mathrm{d}\Sigma), \qquad j = 0, 1, \dots 4, \tag{C.2}$$

where $h = (-ig/\omega)_\beta$ in the case of the collective reservoir model, and $h = (-ig_1/\omega)_\beta$ and $h = (-ig_2/\omega)_\beta$ for the local reservoirs model. We recall (4.3) where $(\cdot)_\beta$ is defined. The square root factor $(u/(1-e^{-\beta u}))^{1/2}$ in (4.3) is infinitely many times differentiable for $u \in \mathbb{R}$ and bounded above by (a constant times) $|u|^{1/2}$. A form factor g such that $h = (-ig/\omega)_\beta$ satisfies (C.2) needs to obey $g(0) = 0$ (recall that $\omega(k) = |k|$) and it needs to decay at infinity. Let $p > 0$ be the strength of the zero and σ the speed of decay, namely, $g(k) = |k|^p (1 + |k|)^{-\sigma} \widetilde{g}(k)$, for some function $\widetilde{g}(k)$ which is four times differentiable w.r.t. its radial component ($r = |k|$) and satisfies $\sup_{k \in \mathbb{R}^3} |\partial_{|k|}^j \widetilde{g}(k)| < \infty$ for $j = 0, \ldots, 4$. Assume that g is real valued (this is not necessary, but it slightly simplifies the exposition). Close to $u = 0$, the singularity structure of h is $\propto |u|^{-1/2+p}$. To have local square integrability of $\partial_u^j h$ at $u = 0$ we thus need that either $-1/2 + p$ is an integer $n \geq 0$, or that $p > j$. Hence $p = (2\ell + 1)/2$, $\ell = 0, 1, 2, \ldots$ or $p > 4$ (as $j = 0, \ldots, 4$). The integrability at $u \to \infty$ is guaranteed for $\sigma > 3/2$.

Note that the above infrared condition is stronger than the infrared condition necessary to apply the polaron transformation, which would only ask for $p > -1/2$ (so that $g_{1,2}/\omega \in L^2(\mathbb{R}^3, \mathrm{d}^3 k)$, which is the condition used to be able to deal with arbitrary sizes of λ_1, λ_2 with the help of the polaron transformation, see Proposition 4.1).

We note that in [13], only a dynamical resonance theory for model with a single reservoir is considered. One must slightly adapt the arguments for the case of two reservoirs to be able to describe our local reservoirs model. An easy way to do this is to use a well-known property of Fock space, the isometric isometry

$$\mathcal{F}(L^2) \otimes \mathcal{F}(L^2) = \mathcal{F}(L^2 \oplus L^2), \qquad \text{where} \quad L^2 \equiv L^2(\mathbb{R} \times S^2).$$

Under this mapping, the formalism of two reservoirs turns into one of a single reservoir (albeit on a different one-particle space). The arguments of [13] leading to the resonance expansion of the propagator (c.f. (4.30)) can then be adapted in a straightforward way to this new single-reservoir setting. We do not present the details of the analysis in the present work.

D   Parameter constraints

The large coupling results of [14, 13] our resonance approach in the current work is based on are stated as follows. Given arbitrary $\lambda_1, \lambda_2 \in \mathbb{R}$, there is a constant $V_0 > 0$ such that if $|V| < V_0$, then the results hold. The upper bound V_0 depends on the fixed λ_1, λ_2. This dependence can be found by tracing the parameters λ_1, λ_2 through the arguments of [14, 13]. We set

$$\widetilde{\gamma} = \gamma/V^2, \quad \theta = \min\{|\hat{\epsilon}|, \widetilde{\gamma}\}, \tag{D.1}$$

where γ and $\hat{\epsilon}$ are given in (2.25) and (2.14), respectively. Note that $\widetilde{\gamma}$ and $\hat{\epsilon}$ depend on λ_1 and λ_2. The following are constraints used to prove the validity of the dynamical resonance theory.

Collective reservoir model. The interaction (4.19) depends only on the difference $\lambda_1 - \lambda_2$ of the coupling constants. Define

$$\xi = |\lambda_1 - \lambda_2|.$$

Let C be a constant which does not depend on V, λ_2, λ_2.

- Validity of the *Born approximation*,

$$|V| \le C(1 + \xi^2)^{-1}. \tag{D.2}$$

This constraint is used to isolate the main dynamics in which the reservoir can be considered in its equilibrium state at all times, i.e., to justify the Born approximation. [Technical remark: the condition is needed to show that $\bar{L}(\eta)$ has spectrum in the lower complex half plane, c.f. Lemma 4.3 of [14]; the main dynamics can then be expressed on $\mathrm{Ran}P_\Omega$.]

- Separation of resonances,

$$|V| \le C \min\{\widetilde{\gamma}\,(1 + \xi^6)^{-1}, \sqrt{\widetilde{\gamma}}\,\xi^{-5}\}. \tag{D.3}$$

This condition ensures that the effective complex dimer energy differences, i.e., the resonances are well separated. Then they determine three decaying directions (in the dimer Liouville space) and one equilibrium direction. If this condition is not satisfied, then one must develop a theory of overlapping resonances [22, 20].
The resonances are the complex a_0, $a_\pm$, (4.40) and $a_0' = 0$. Rescaled by V^{-2}, their separation (smallest distance among them) is $\propto \widetilde{\gamma} = \widetilde{\gamma}(\lambda_1, \lambda_2)$. Even if the real part $\hat{\epsilon} \pm x_{\mathrm{LS}}$ of $a_\pm$ is large, shifting those two resonances horizontally far away from the origin, one resonance (a_0) stays at a distance $\widetilde{\gamma}$ from $a_0' = 0$. The separation of resonances (rescaled by V^{-2}) must persist for perturbations small in V, hence the above upper bound on V. [Technical remark: This condition is used to guarantee that A_z is close to the level shift operator in Lemma 3.1 of [13].]

- No backreaction on the dimer,

$$|V| \le C \min\{\theta, \sqrt{\theta}(1 + \xi^6)^{-1}\}. \tag{D.4}$$

The stationary states of the uncoupled dimer-reservoir system are (superpositions of) states with the dimer in a dimer-energy eigenstate and the reservoir in equilibrium. The above condition ensures that away from these states, the coupled dynamics is dispersive (local observables decay sufficiently quickly in time). The dispersiveness estimates are obtained separately for different stationary dimer Bohr energies, so they involve their separation, $\hat{\epsilon}$ (on which θ depends). [Technical remark: This condition is used to prove the Limiting Absorption Principles of the interacting resolvent, in particular when reduced to $\mathrm{Ran}P_e^\perp$, Theorem A.1 in [13].]

Discussion. Consider spectral functions of the form (2.28), $J(\omega) = A\omega^{2p+2}\mathrm{e}^{-\omega/\omega_c}$, with p as in (2.9).

(1) Consider $\xi \ll 1$. We now show that

$$\gamma_{\mathrm{col}} \le C \begin{cases} \xi^6(\hat{\epsilon})^{2p}\min\{\mathrm{e}^{-|\hat{\epsilon}|/\omega_c}, |\hat{\epsilon}|^{-1}\} & \text{if } |\hat{\epsilon}| \ge C\xi^2, \\ \xi^2|\hat{\epsilon}|^{2p+1} & \text{if } |\hat{\epsilon}| \le C\xi^2. \end{cases} \tag{D.5}$$

For small ξ, we have $\widetilde{\gamma} \propto \frac{\xi^2}{\hat{\epsilon}^2} J(|\hat{\epsilon}|) \coth(\beta|\hat{\epsilon}|/2)$, see Section 5 of [18]. Taking into account the form of the spectral density (2.28), we obtain

$$\gamma_{\mathrm{col}} = V^2\widetilde{\gamma} \propto V^2\xi^2(\hat{\epsilon})^{2p}\mathrm{e}^{-|\hat{\epsilon}|/\omega_c}\coth(\beta|\hat{\epsilon}|/2). \tag{D.6}$$

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Consider two cases:

(a) $|\hat{\epsilon}| \geq C\xi^2$ hence $\theta = \xi^2$. The conditions (D.2) – (D.4) become $|V| \leq C\xi^2$ and from (D.6) we obtain the first estimate in (D.5).

(b) $|\hat{\epsilon}| \leq C\xi^2$, so that $\theta = |\hat{\epsilon}|$. The conditions (D.2) – (D.4) become $|V| \leq C|\hat{\epsilon}|$ so $\gamma_{\mathrm{col}} \leq C\xi^2|\hat{\epsilon}|^{2p+1}$.

(2) Consider $\xi \approx 1$. The conditions (D.2) – (D.4) become $|V| \leq \min\{\widetilde{\gamma}, \sqrt{\widetilde{\gamma}}, |\hat{\epsilon}|, \sqrt{|\hat{\epsilon}|}\}$.

(3) Consider $\xi \gg 1$. From (2.25) we expect that $\widetilde{\gamma} \propto \mathrm{e}^{-c\xi^2}$ for some $c > 0$. The conditions (D.2) – (D.4) become $|V| \leq C\mathrm{e}^{-c\xi^2}$ and therefore $\gamma_{\mathrm{col}} \leq C\mathrm{e}^{-c\xi^2}$ is extremely tiny.

Conclusion. Sizeable values of γ_{col} will be obtained in the regime $\xi \approx 1$ only, that is, when the difference of λ_1 and λ_2 is not too large nor too small. For $\lambda_1 \approx \lambda_2$, the dynamical process is suppressed (weakly, γ_{col} is proportional to a power of $|\lambda_1 - \lambda_2|$) because for $\lambda_1 = \lambda_2$ there is no relaxation or decoherence at all. For $|\lambda_1 - \lambda_2| \gg 1$ the dynamical process is is strongly suppressed ($\gamma_{\mathrm{col}} \propto \mathrm{e}^{-c|\lambda_1-\lambda_2|^2}$), which is an effect analogous to Anderson localization.

Remark. If we use the expression (2.35) for γ_{col} in the Marcus regime, we have $\gamma_{\mathrm{col}} \leq CV^2/\xi$. The above constraints (D.2) – (D.4) on V give an upper bound on γ_{col},

$$\gamma_{\mathrm{col}} \leq C \begin{cases} \xi & \text{for } \xi \ll 1, \\ \min\{\widetilde{\gamma}, \sqrt{\widetilde{\gamma}}, |\hat{\epsilon}|, \sqrt{|\hat{\epsilon}|}\} & \text{for } \xi \approx 1, \qquad \text{(Marcus regime)} \\ \mathrm{e}^{-c\xi^2} & \text{for } \xi \gg 1. \end{cases} \qquad \text{(D.7)}$$

These upper bounds are qualitatively correct (they coincide qualitatively with the ones obtained from the true expression (2.25) for γ_{col}, even though for small ξ, the power of the upper bound is different).

Local reservoirs model. Here the bounds (D.2)-(D.4) need to be verified with $\xi = \lambda_1$ and $\xi = \lambda_2$.

E   Reservoirs and continuous mode limits

A reservoir of vibrational modes is typically modeled by a collection of (independent) quantum oscillators with Hamiltonian ($\hbar = 1$)

$$H_N = \sum_{k=1}^{N} \omega_k a_k^\dagger a_k, \qquad (\text{E.1})$$

with $a_k a_\ell^\dagger - a_\ell^\dagger a_k = \delta_{k,\ell}$ (Kronecker symbol). In the context of a *'molecular reservoir'*, one has N (protein, solvent...) atoms in the environment, each one being modeled by three degrees of freedom, i.e., by a three-dimensional linear quantum oscillator with frequencies $\omega_{n,d}$, $n = 1, \ldots, N$, $d = 1, 2, 3$. The Hamiltonian of the (finite mode) reservoir could then be written as in (E.1) with either N replaced by $3N$ or it could be written as a sum over $\vec{k} = (k_1, k_2, k_3)$. In a *'structured environment'*, say, given by a periodic structure, by phonons or photons, the index $\vec{k}$ is the wave vector and has associated frequency $\omega_{\vec{k}}$. This fixes a relation between

k and ω, the dispersion relation (e.g. $\omega = |k|$ for acoustic phonons or photons). However, the frequencies present in a molecular reservoir may be more 'random'. One can list them increasingly as $\omega_1 \leq \omega_2 \leq \cdots \leq \omega_n$, but there is no inherent relation between the index j and the value ω_j. The defining property for a molecular reservoir is the *fraction among all oscillators having a given frequency*. It is determined by a function $\varrho(\omega)$ such that for any set $I \subset \mathbb{R}_+$, the quantity $\int_I \varrho(\omega)\mathrm{d}\omega$ is the proportion of all oscillators having frequencies lying in I. In particular, $\int_0^\infty \varrho(\omega)\mathrm{d}\omega = 1$. The function ϱ is the *frequency density of the molecular environment*.

Mathematically, the treatment of molecular and structured reservoirs is the same. Our method does not rely on the presence or absence of a dispersion relation. The only quantity that matters is the spectral function $J(\omega)$, which is defined via the correlation function of the reservoir, c.f. (2.6). The *explicit relation* between the spectral function J and the form factor g will depend on the nature of the reservoir (dispersion relation or frequency density). For instance, for three dimensional phonons or photons with $\omega_k = |k|$, we have

$$J(\omega) = \frac{\pi}{2}\omega^2 \int_{S^2} |g(\omega, \Sigma)|^2 \mathrm{d}\Sigma \tag{E.2}$$

(where g is represented in spherical coordinates of $k \in \mathbb{R}^3$). For a molecular reservoir with frequency density $\varrho(k)$,

$$J(\omega) = \pi \varrho(\omega)|g(\omega)|^2. \tag{E.3}$$

However, in either case, the relevant physical characteristics of the reservoir are condensed into the function $J(\omega)$, which is typically of the form (2.8) or (2.28).

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