Decoherence-Assisted Transport in a Dimer System

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The dynamics of a dimer coupled to two different environments, each in a spin star configuration under
the influence of decoherence, is studied. The exact analytical expression for the transition probability in
the dimer system is obtained for different situations, i.e., independent and correlated environments. In all
cases considered, it is shown that there exist well-defined ranges of parameters for which decoherent
interaction with the environment assists energy transfer in the dimer system. In particular, we find that
correlated environments can assist energy transfer more efficiently than separate baths.

The processes of energy and information transfer in
quantum networks play an important role for quantum
communication and quantum computation. In realistic
physical situations, the unavoidable interaction with the
environment leads to decoherence and dissipation, which
typically play a coherence-destructive role [1]. However,
recently, ultrafast spectroscopic techniques have been
claimed to reveal long-lasting quantum coherence in bio-
logical systems, including the photosynthetic light-
harvesting complexes of a species of green sulfur bacteria
[2,3], a species of purple bacteria [4], and two species of
marine cryptophyte algae [5]. Pigment-protein light-
harvesting antennas in the photosynthetic complex transfer
excitonic energy rapidly and efficiently [6] through a series
of electronic excitations to the reaction center [7]. The
efficiency of the energy transfer through the network of
chromophores and the evidence of quantum coherence
have led to discussion about the role of the environment
in the quantum transfer process and the degree to which it
may contribute to the transport efficiency.

It has been shown that, in a simple model of an aggregate
of monomers interacting through dipole-dipole forces with
realistic coupling strengths, quantum and classical coher-
ent transport are comparable [8]. At the same time, there is
much activity proposing mechanisms for environment-
assisted excitonic energy transport in quantum networks,
including those under the broad headings of noise-assisted
transport [9] and oscillation-enhanced transport [10]. The
possibility that quantum entanglement may enhance trans-
port has also been discussed [11].

Modeling the complexity of the environment is a chal-
lenge [12]. The protein-solvent environment interacts
strongly with the pigments due to its polarity and as a result
can have a significant effect on the quantum dynamics [13],
which will therefore in general be non-Markovian [14].
Such non-Markovian effects have widely been taken into
account [14,15], but so far, all have been within spin-boson

models of excitons within a protein medium. Any biological
system is always in contact with a bosonic environment.
However, the interaction with a more structured environ-
ment such as a spin bath is more likely to assist quantum
efficiency. Spin baths are natural candidates because the
reduced dynamics which they induce are intrinsically non-
Markovian [16] and the relevance of the electron-nuclear
spin interactions in photosynthesis (especially in reaction
center dynamics) has been recognized for a long time [17].

In this Letter, we are going to study the simplest elec-
tronic energy transfer system, namely, a dimer coupled
to a spin bath. The Hamiltonian of the dimer is given by
$H_d = \varepsilon_1|1\rangle\langle1| + \varepsilon_2|2\rangle\langle2| + J(|1\rangle\langle2| + |2\rangle\langle1|)$, where ε_i are
the energy levels of the dimer and J is the amplitude of
transition. It is well-known that, in the absence of an
environment, if the initial excitation is in level 1, then the
maximum of the probability of transition to level 2,
$[P_{1\rightarrow2}(t)]$, will be given by $\text{Max}[P_{1\rightarrow2}(t)] = J^2/(J^2 + \Delta^2)$, where Δ is half of the energy difference between the
levels of a dimer $[\Delta = (\varepsilon_2 - \varepsilon_1)/2]$. This means that, only
in the case $\varepsilon_1 = \varepsilon_2$, we can say that excitation is trans-
ferred with certainty $[P_{1\rightarrow2}(t_0) = 1]$ at the time moment
$t_0 = \pi/2J$. In all other cases ($\varepsilon_1 \neq \varepsilon_2$), the probability of
transition is always smaller than 1. The aim of this paper is
to show that, in a generic case ($\varepsilon_1 \neq \varepsilon_2$), for a dimer in
contact with two spin environments, decoherence can en-
hance energy transfer.

For the sake of simplicity and exact solvability, the
environment to which the dimer couples will be modeled
as a bath of independent spins $1/2$ in a spin star configu-
ration [16]. Figure 1 depicts the dimer in contact with the
two baths. Thus, the Hamiltonian of the total system has
the following form:

$$H = H_d + H_{B_1} + H_{B_2} + H_{dB_1} + H_{dB_2}.$$

As it was mentioned above, each environment B_i consists
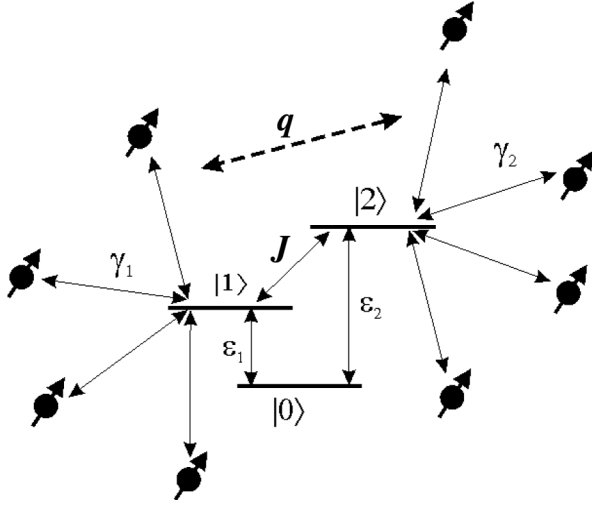of N_i particles ($i = 1, 2$) with spin $1/2$:

FIG. 1. Scheme of the dimer coupled to two decoherent environments in a spin star configuration. A dimer has energy levels $\varepsilon_1 \neq \varepsilon_2$ and amplitude of transition probability J. Each level of the dimer $|1\rangle$ and $|2\rangle$ is in contact with a bath of spins with coupling constants γ_1 and γ_2, respectively. The dashed double arrow denotes the possibility of correlations between the baths through the Ising-like interaction $\sum_{k,m}\sigma_z^{k,1}\sigma_z^{m,2}$ with strength q.

$$H_{B_i} = \alpha_i \sum_{k=1}^{N_i} \frac{\sigma_z^{k,i}}{2},$$

where $\sigma_z^{k,i}$ are the well-known Pauli matrices. The decoherent interaction between the dimer and the baths is described by

$$H_{dB_i} = \sum_{k=1}^{N_i} \gamma_i |i\rangle\langle i| \frac{\sigma_z^{k,i}}{2},$$

where γ_i denotes the strength of the interaction of the system with the bath. For a spin bath in such a configuration, it is convenient to define collective spin operators:

$$S_i^z = \sum_{k=1}^{N_i} \frac{\sigma_z^{k,i}}{2}.$$

In this notation, the total Hamiltonian can be written in the form

$$H = J(|1\rangle\langle 2| + |2\rangle\langle 1|) + \sum_{i=1}^{2} (\varepsilon_i |i\rangle\langle i| + \alpha_i S_i^z + \gamma_i |i\rangle\langle i| S_i^z).$$

For the description of the dimer system, we express the projectors $|i\rangle\langle j|$ through the Pauli matrices, i.e.,

$$|1\rangle\langle 1| = \frac{1_2 - \sigma_z}{2}, \qquad |2\rangle\langle 2| = \frac{1_2 + \sigma_z}{2},$$
$$|2\rangle\langle 1| = \sigma^+.$$

Thus, the total Hamiltonian can be written in the following form:

$$H = \delta(S_1^z, S_2^z)1_2 + \left(\frac{\varepsilon_2 - \varepsilon_1}{2} - \frac{\gamma_1 S_1^z - \gamma_2 S_2^z}{2}\right)\sigma_z + J\sigma_x.$$

Let us first consider the simplest special case of both environments at zero temperature. Obviously, in this case, in both reservoirs all spins are in the ground state. Hence, the initial state of the bath is a pure state and is described by the following wave function:

$$|\Psi_B(0)\rangle = \left|\frac{N_1}{2}, -\frac{N_1}{2}\right\rangle \otimes \left|\frac{N_2}{2}, -\frac{N_2}{2}\right\rangle,$$

where the vector $|j, m\rangle$ denotes the well-known eigenvectors of the angular momentum operator,

$$S^2|j, m\rangle = j(j + 1)|j, m\rangle, \qquad S_z|j, m\rangle = m|j, m\rangle,$$

and $S^2 = S_x^2 + S_y^2 + S_z^2$, for $j = 0, \ldots, N/2$ and $m = -j, \ldots, 0, \ldots, j$.

Using the fact that the Hamiltonian of the reservoirs H_{B_i} commutes with the Hamiltonian of the interaction H_{dB_j}, the state of the system will be always of the form

$$|\Psi_{\text{Total}}(t)\rangle = \sum_{i=1}^{2} c_i(t)|i\rangle \otimes |\Psi_B(0)\rangle.$$

We assume that, at time $t = 0$, the excitation is in level 1 of the dimer, i.e., $c_1(0) = 1$ and $c_2(0) = 0$. The corresponding Schrödinger equation can be easily integrated, and the probability of transition given by the dynamics of the coefficient $|c_2(t)|^2$ is found to be

$$P_{1\to 2}(t) = |c_2(t)|^2 = \frac{J^2}{J^2 + \Delta^2} \sin^2(t\sqrt{J^2 + \Delta^2}),$$

where

$$\Delta = \frac{\varepsilon_2 - \varepsilon_1}{2} + \frac{\gamma_1 N_1 - \gamma_2 N_2}{4}.$$

It is obvious now that, for specially chosen parameters of the baths (γ_i or N_i), it is possible to compensate for the energy difference between two levels of the dimer, such that $\Delta = 0$ and $\text{Max}[P_{1\to 2}(t)] = 1$, namely, by setting

$$\frac{\varepsilon_1 - \varepsilon_2}{2} = \frac{\gamma_1 N_1 - \gamma_2 N_2}{4}.$$

This implies a very simple mechanism of increasing the probability of transition in the dimer.

Our main interest, of course, is in the generic case of the dimer coupled to baths at nonzero temperatures. In this case, the initial state of the bath is given by the canonical distribution

$$\rho_B(0) = \prod_{i=1}^{2} \frac{1}{Z_i} e^{-\beta\alpha_i S_i^z},$$

where Z_i is the partition function of the corresponding bath,

$$Z_i = \sum_{j_i=0}^{N_i/2} \sum_{m_i=-j_i}^{j_i} \nu(N_i, j_i) \langle j_i, m_i | e^{-\beta\alpha_i S_i^z} | j_i, m_i \rangle$$

$$= \sum_{j_i=0}^{N_i/2} \nu(N_i, j_i) \frac{\sinh\beta\alpha_i(j_i + \frac{1}{2})}{\sinh(\beta\alpha_i/2)},$$

β is the inverse temperature, and $\nu(N_i, j_i)$ denotes the degeneracy of the spin bath [18,19].

Using the commutativity of the Hamiltonian of interaction H_{dB_j} and the total Hamiltonian H, it is possible to show that, in the non-zero-temperature case, the transition probability is

$$P_{1\to2}(t) = \text{Tr}_B[\langle 2|U(t)|1\rangle\rho_B(0)\langle 1|U(t)^\dagger|2\rangle]$$

$$= \frac{1}{Z_1 Z_2} \sum_{j_1=0}^{N_1/2} \sum_{m_1=-j_1}^{j_1} \sum_{j_2=0}^{N_2/2} \sum_{m_2=-j_2}^{j_2} \frac{\nu(N_1, j_1)\nu(N_2, j_2)J^2}{J^2 + \Delta_{m_1,m_2}^2}$$

$$\times \sin^2(t\sqrt{J^2 + \Delta_{m_1,m_2}^2})e^{-\beta\alpha_1 m_1 - \beta\alpha_2 m_2},$$

where Δ_{m_1,m_2} is given by

$$\Delta_{m_1,m_2} = \frac{\varepsilon_2 - \varepsilon_1}{2} - \frac{\gamma_1 m_1 - \gamma_2 m_2}{2}.$$

In Fig. 2, the probability of transition in the dimer system as a function of time and coupling constant is presented. In this case, only the upper level of the dimer is coupled to a spin bath with coupling constant $\gamma_2 = \gamma$. In Fig. 2(a), we show the results for a spin bath at 77 K, whereas, in Fig. 2(b), the temperature of the bath is 300 K. For both bath temperatures, one can see that the maximum of the probability of transition is achieved for a nonvanishing interaction with the spin environment. The transfer of energy is enhanced when the bath configurations that contribute to the decrease of the distance between the levels of the dimer prevail. The increased transition rate occurs on time scales of the order of a few hundred femtoseconds, which corresponds to experimental observation [2,3] and theoretical predictions [20]. This means that, not only at zero temperature, but also in more realistic cases, decoherence assists the energy transfer in the dimer system for the class of models which we are considering here.

The spin bath model allows us to investigate analytically the influence of the correlation between environments on the probability of transition. To this end, we introduce an Ising-type interaction between environments with strength q, so that the bath Hamiltonian H_B assumes the following form:

$$H_B = \alpha_1 S_1^z + \alpha_2 S_2^z + q S_1^z S_2^z.$$

In the special case of environments that are correlated and at zero temperature, it is easy to see that the probability of transition is simply given by

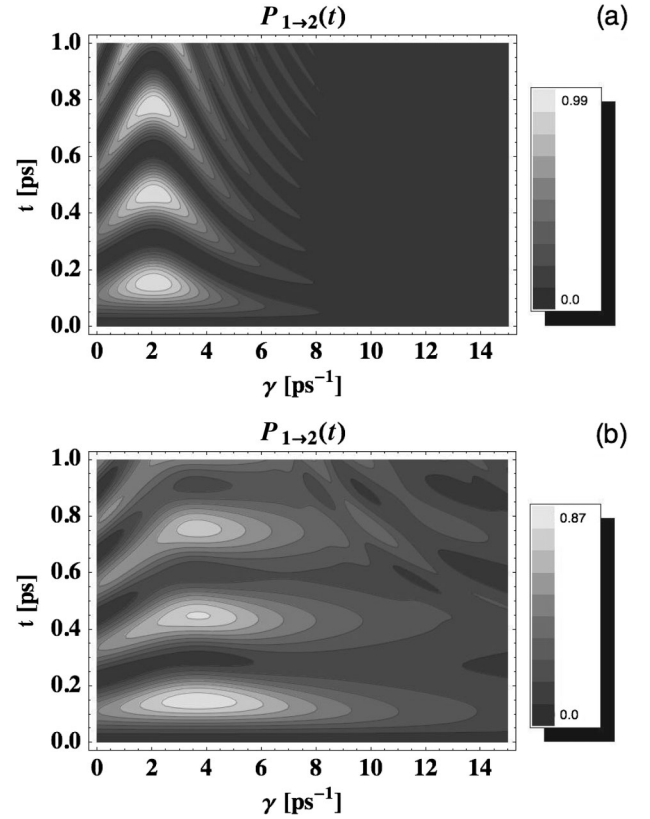$$P_{1\to2}(t) = \frac{J^2}{J^2 + \Delta_0^2} \sin^2(t\sqrt{J^2 + \Delta_0^2}),$$

FIG. 2.   Probability of transition $P_{1\to2}(t)$ in the dimer system with the upper level coupled to a spin bath ($\gamma_1 = 0$) as a function of time and the coupling constant to the spin bath ($\gamma_2 = \gamma$). The temperature of the spin bath in Fig. 2(a) is 77 K, while, in Fig. 2(b), it is 300 K. For both figures, the parameters are chosen to be $N_2 = 20$, $\alpha_2 = 250$ ps^{-1}, $J = 10$ ps^{-1}, and $\varepsilon_2 - \varepsilon_1 = 20$ ps^{-1}.

where

$$\Delta_0 = \frac{\varepsilon_2 - \varepsilon_1}{2} + \langle \Psi_B(0) \left| \frac{\gamma_2 S_2^z - \gamma_1 S_1^z}{2} \right| \Psi_B(0)\rangle.$$

The wave vector $|\Psi_B(0)\rangle$ denotes the initial state of the bath; in this particular case (zero-temperature), it would be the ground state of the Hamiltonian H_B. Because of the interaction between baths, the ground state of the Hamiltonian H_B will depend on parameters α_1, α_2, and q of the Hamiltonian H_B. We have shown that the state vector $|\Psi_B(0)\rangle$ will be given by

$$|\Psi_B(0)\rangle = \begin{cases} \left|\frac{N_1}{2}, -\frac{N_1}{2}\right\rangle \otimes \left|\frac{N_2}{2}, -\frac{N_2}{2}\right\rangle & \text{for } q < q_0, \\ \left|\frac{N_1}{2}, -\frac{N_1}{2}\right\rangle \otimes \left|\frac{N_2}{2}, \frac{N_2}{2}\right\rangle & \text{for } q > q_0, \alpha_1 > \alpha_2, \\ \left|\frac{N_1}{2}, \frac{N_1}{2}\right\rangle \otimes \left|\frac{N_2}{2}, -\frac{N_2}{2}\right\rangle & \text{for } q > q_0, \alpha_1 < \alpha_2, \end{cases}$$

where $q_0 = 2\text{Min}(\frac{\alpha_1}{N_2}, \frac{\alpha_2}{N_1})$. In the case of degeneracy of the parameters, e.g., $q = q_0$ or $\alpha_1 = \alpha_2$, one should take the normalized linear combination of the corresponding

ground states. For example, if $q > q_0$ and $\alpha_1 = \alpha_2$, then the ground state will be given by

$$|\Psi_B(0)\rangle = \cos\theta \left| \frac{N_1}{2}, -\frac{N_1}{2} \right\rangle \otimes \left| \frac{N_2}{2}, \frac{N_2}{2} \right\rangle$$
$$+ \sin\theta e^{i\phi} \left| \frac{N_1}{2}, \frac{N_1}{2} \right\rangle \otimes \left| \frac{N_2}{2}, -\frac{N_2}{2} \right\rangle,$$

where $0 \le \theta \le \pi$ and $0 \le \phi < 2\pi$.

One can easily formulate conditions under which the interaction with the baths will assist transitions in the system ($\Delta_0 = 0$), namely,

$$\frac{\varepsilon_2 - \varepsilon_1}{2} = \begin{cases} (\gamma_1 N_1 - \gamma_2 N_2)/4 & \text{for } q < q_0, \\ -(\gamma_1 N_1 + \gamma_2 N_2)/4 & \text{for } q > q_0, \alpha_1 > \alpha_2, \varepsilon_2 < \varepsilon_1, \\ (\gamma_1 N_1 + \gamma_2 N_2)/4 & \text{for } q > q_0, \alpha_1 < \alpha_2, \varepsilon_2 > \varepsilon_1. \end{cases}$$

In the most general case considered here, i.e., correlated environments at nonzero temperature, the probability of transition is found to be

$$P_{1\to2}(t) = \frac{1}{Z} \sum_{j_1=0}^{N_1/2} \sum_{m_1=-j_1}^{j_1} \sum_{j_2=0}^{N_2/2} \sum_{m_2=-j_2}^{j_2} \frac{\nu(N_1, j_1)\nu(N_2, j_2)J^2}{J^2 + \Delta_{m_1,m_2}^2}$$
$$\times \sin^2(t\sqrt{J^2 + \Delta_{m_1,m_2}^2})e^{-\beta\alpha_1 m_1 - \beta\alpha_2 m_2 - \beta q m_1 m_2},$$

where Δ_{m_1,m_2} is given by

$$\Delta_{m_1,m_2} = \frac{\varepsilon_2 - \varepsilon_1}{2} + \frac{\gamma_2 m_2 - \gamma_1 m_1}{2}.$$

Figure 3 addresses the question of the influence of correlations between the environments on the energy transfer in the non-zero-temperature case. It shows the maximum of the probability of transition as a function of the coupling strengths and correlation parameters for two different bath temperatures: 77 K in Fig. 3(a) and 300 K in Fig. 3(b). The introduction of correlations between the baths results in an increase in the probability of transition in a well-defined region of the coupling parameter. Interestingly, in the case of higher temperatures, a stronger correlation between the baths is required to observe an increase of the probability of transition. For both temperatures, the maximum of the transition probability was found on time scales of the order of few hundreds of femtoseconds. It is important to stress that, for the simple model considered here, the maximum of the transition probability reaches 99% at 77 K and 88% at 300 K.

In conclusion, in this Letter, we have investigated the possible relevance of a spin environment in assisting energy transfer in a dimer system. Even for a very simple model with biologically applicable parameter ranges and time scales, it is found that the transition probability in the dimer is dramatically increased. In particular, we have demonstrated that, for this class of models, correlations between the environments contribute to the increase of the quantum efficiency of transport. Interestingly, for a dimer
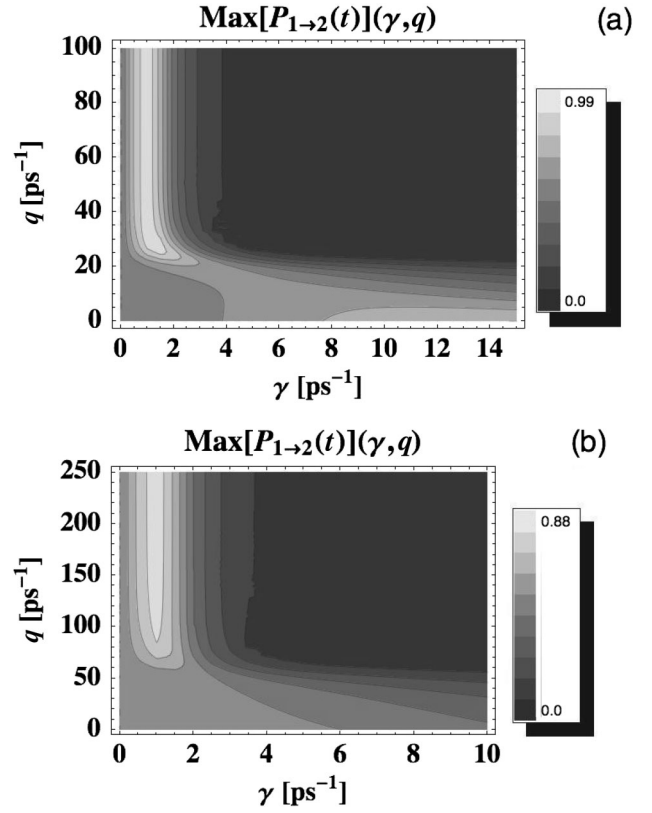

FIG. 3. Maximum of the probability of transition $\text{Max}[P_{1\to2}(t)]$ for a dimer coupled to two spin baths as a function of the correlations q between the baths and the coupling constants $\gamma_1 = \gamma_2 = \gamma$ of the interaction with the baths in the non-zero-temperature case. In Fig. 3(a), the temperature of the baths is 77 K, while, in Fig. 3(b), it is 300 K. For both figures, the parameters are $N_1 = 22$, $N_2 = 20$, $\alpha_1 = \alpha_2 = 250 \text{ ps}^{-1}$, $J = 10 \text{ ps}^{-1}$, and $\varepsilon_2 - \varepsilon_1 = 20 \text{ ps}^{-1}$.

coupled to two different baths, introducing correlations between the baths improves quantum transport. These promising results motivate further study of energy transfer networks and more complex environmental models.

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