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 biological systems, including the photosynthetic light-harvesting complexes of a species of green sulphur bacteria [2, 3], a species of purple bacteria [4], and two species of marine cryptophyte algae [5]. Pigment-protein light-harvesting antenna in the photosynthetic complex transfer excitonic energy rapidly and efficiently [6] through a series of electronic excitations to the reaction centre [7]. The efficiency of the energy transfer through the network of chromophores and the evidence of quantum coherence has 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 coherent transport are comparable [8]. At the same time there is much activity proposing mechanisms for environment-assisted excitonic energy transfer in quantum networks, including under the broad headings of noise-assisted transport [9] and oscillation-enhanced transport [10]. The possibility that quantum entanglement may enhance transport has also been discussed [11].

Modeling the complexity of the environment is a challenge [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 within spin-boson models of excitons within a protein medium. Any biological system is always in a contact with a bosonic environment. However, the interaction with a more structured environment 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 centers dynamics) has been recognized for a long time [17].

In this paper we are going to study the simplest electronic energy transfer system, namely, a dimer coupled to a spin bath. The Hamiltonian of the dimer is given by $H_d = \varepsilon_1 |1\rangle\langle 1| + \varepsilon_2 |2\rangle\langle 2| + J (|1\rangle\langle 2| + |2\rangle\langle 1|)$, where $\varepsilon_i$ 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 ($P_{1\rightarrow 2}(t)$), will be given by $\text{Max} [P_{1\rightarrow 2}(t)] = J^2/(J^2 + \Delta^2)$, where $\Delta$ 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 transferred with certainty ($P_{1\rightarrow 2}(t_0) = 1$) 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 one. 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 enhance energy transfer.

For the sake of simplicity and exact solvability the environ-

![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 $\gamma$.](image)
ment to which the dimer couples will be modeled as a bath of independent spins 1/2 in a spin star configuration [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:

\[ H_{B_i} = \alpha_i \sum_{k=1}^{N_i} \sigma^{k,i}_z. \]

where \( \sigma^{k,i}_z \) are the well-known Pauli matrices. The decoherent interaction between the dimer and the baths is described by:

\[ H_{dB_i} = \sum_{k=1}^{N_i} \gamma_i |i\rangle \langle i| \sigma^{k,i}_z. \]

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

\[ S_i^z = \sum_{k=1}^{N_i} \sigma^{k,i}_z. \]

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

\[ H = J \left( |1\rangle \langle 2| + |2\rangle \langle 1| \right) + \sum_{i=1}^2 \left( \epsilon_i |i\rangle \langle i| + \alpha_i S_i^z + \gamma_i |i\rangle \langle i| S_i^z \right). \]

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

\[ |1\rangle \langle 1| = \frac{1}{2} - \sigma_z, \quad |2\rangle \langle 2| = \frac{1}{2} + \sigma_z, \quad |2\rangle \langle 1| = \sigma^+. \]

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

\[ H = \delta \left( S_1^z, S_2^z \right) \frac{1}{2} + \left( \frac{\epsilon_2 - \epsilon_1}{2} - \frac{\gamma_1 S_1^z - \gamma_2 S_2^z}{2} \right) \sigma_z + J \sigma_x. \]

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:

\[ |\Psi_B(0)\rangle = \frac{N_1}{2} |\frac{N_1}{2}, -\frac{N_2}{2} \rangle \otimes \frac{N_2}{2} |\frac{N_2}{2}, -\frac{N_1}{2} \rangle, \]

where the vector \(|j, m\rangle\) denotes the well known eigenvectors of the angular momentum operator, \(S^2|j, m\rangle = j(j+1)|j, m\rangle, S_z|j, m\rangle = m|j, m\rangle, S^2|j, m\rangle = S_x^2 + S_y^2 + S_z^2, \)

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:

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

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

\[ P_{1\rightarrow 2}(t) = |c_2(t)|^2 = \frac{J^2}{J^2 + \Delta^2} \sin^2 \left( t \sqrt{J^2 + \Delta^2} \right), \]

where

\[ \Delta = \frac{\epsilon_2 - \epsilon_1}{2} + \frac{\gamma_1 N_1 - \gamma_2 N_2}{4}. \]

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

\[ \frac{\epsilon_1 - \epsilon_2}{2} = \frac{\gamma_1 N_1 - \gamma_2 N_2}{4}. \]

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 non-zero 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.

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

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

\( \beta \) 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 \( H_{dB_i} \) and the total Hamiltonian \( H \) it is possible to show that in the non-zero temperature case the transition probability is:
$$P_{1\rightarrow 2}(t) = \text{Tr}_B \left[ (2|U(t)|1)\rho_B(0)(1|U(t)|2) \right]$$

$$= \frac{1}{Z_1Z_2} \sum_{j_1=0}^{N_1/2} \sum_{m_1=-j_1}^{j_1} \sum_{j_2=0}^{N_2/2} \sum_{m_2=-j_2}^{j_2} \frac{\nu(N_1,j_1)\nu(N_2,j_2)J^2}{J^2 + \Delta_{m_1,m_2}^2} \sin^2 \left( t\sqrt{J^2 + \Delta_m^2} \right) e^{-\beta m_1 - \beta m_2},$$

between the levels of the dimer prevail. The increased transition rate occurs on timescales 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 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:

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

where

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

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 $H_B$. Due to the interaction between baths the ground state of the Hamiltonian $H_B$ will depend on parameters $\alpha_1, \alpha_2$ and $q$ of the Hamiltonian $H_B$. We have shown that the state vector $|\Psi_B(0)\rangle$ will be given by:

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

where $q_0 = 2\text{Min} \left( \frac{\alpha_1}{\alpha_2}, \frac{\alpha_2}{\alpha_1} \right)$. 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:

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

where $0 \leq \theta \leq \pi$ and $0 \leq \phi < 2\pi$.
One can easily formulate conditions under which the interaction with the baths will assist transitions in the system ($\Delta_0 = 0$), namely

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

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

$$P_{1 \rightarrow 2}(t) = \frac{1}{2} \sum_{j_1=0}^{N_1/2} \sum_{j_1}^{N_2/2} \sum_{j_2}^{N_2/2} \sum_{m_1=-j_1}^{N_1} \sum_{m_2=-j_2}^{N_2} \frac{\nu(N_1,j_1)\nu(N_2,j_2)}{J^2 + \Delta_{m_1,m_2}^2} \sin^2 \left( t \sqrt{J^2 + \Delta_{m_1,m_2}^2} \right) e^{-\beta\varepsilon_{m_1} - \beta\varepsilon_{m_2} - \beta\gamma m_1 m_2},$$

where $\Delta_{m_1,m_2}$ 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 parameter for two different bath temperatures: 77K in Fig. 3(a) and 300K 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 timescales 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 77K and 88% at 300K.

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 timescales, 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 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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