Exciton dynamics in a quantum mechanical bath

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New theory is needed to explain recent ultrafast experiments on the exciton dynamics in complex environments, such as biological systems or conjugated polymers. In particular, the commonly used approximation (in for example Redfield theory and quantum master equations) of a fast bath is invalid. Our calculations show how a more complete treatment of the bath influences exciton dynamics and nonlinear optical observables.

Introduction Absorption of light in complex materials such as biological light-harvesting systems, DNA, molecular aggregates and conjugated polymers creates excitons. The transport of energy is determined by the nature of these excitons, which depends on the structure of the light-absorbing molecules (also called chromophores), as well as on their interaction with the surrounding environment. Two limits of exciton transport can occur. In the strongly quantum mechanical case, where the effect of the environment is relatively weak, the exciton moves coherently through the network of chromophore molecules. In a linear system, the coherent mechanism leads to ballistic, wave-like transport. In any geometry, this form of transport is typically faster than the incoherent, diffusive hopping. The latter results when the effect of the environment is strong, destroying the quantum mechanical communication between chromophores. The exciton transport can be studied on a femtosecond time scale using nonlinear optics with short laser pulses. To correcly model these experiments, it is crucial to properly include the time scale of the dynamics in the complex environment.

Model A typical exciton system can be described by a Hamiltonian that includes a collection of chromophores, their coupling to eachother, and the effect of the environment on the transition frequency of each chromophore. It can be written as

$$H = \sum_n \epsilon_n c_n^\dagger c_n + \sum_{nn'} J_{nn'} c_n^\dagger c_{n'} - \sum_{n,j} g_{n,j} c_n^\dagger c_n x_j + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2 x_j^2}{2} \right). \tag{1}$$

Here, the chromophores are labeled with indices n and n', which run from 1 to the number of chromophores N. Creation and annihilation operators for these modes are denoted $c^\dagger$ and c, respectively. The environment is modeled as a set of infinitely many harmonic oscillators, labeled by an index j, with coordinates x_j, momenta p_j, masses m_j and frequencies ω_j. Because the coupling is linear in the harmonic coordinates, all information about the effect of the bath on the exciton system is contained in the spectral densities

$$\mathcal{J}_{nn'}(\omega) = \sum_j \frac{g_{n,j} g_{n',j}}{2m_j \omega_j} \delta(\omega - \omega_j). \tag{2}$$

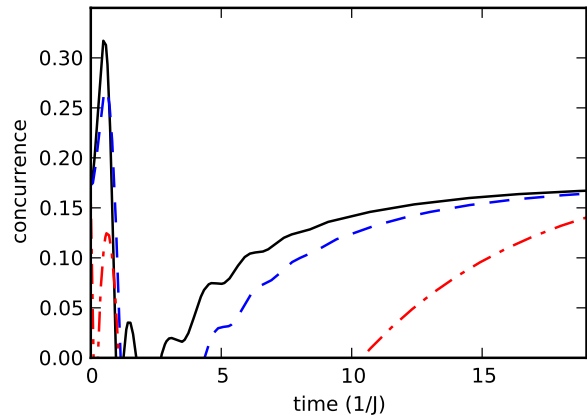A useful model for the spectral densities is given by the overdamped Brownian oscillator,

FIG. 1. Time evolution of the entanglement of two qubits after a pulse has been applied to the equilibrium state. The solid line shows the result of the full calculation, while the system-bath coherence at $t = 0$ was neglected in the results presented as a dashed line. The dash-dotted line shows the Redfield result (from Ref. 3).

$$\mathcal{J}_{nn'}(\omega) = 2\lambda_{nn'} \gamma_{nn'} \frac{\omega \gamma_{nn'}}{\gamma_{nn'}^2 + \omega^2}. \tag{3}$$

This model includes the time scale of the environment through the parameters $\gamma_{nn'}$, and models environment-induced fluctuations as well as dissipation.

Results In the often employed Markovian approximation, one assumes that the time scale of the environmental dynamics, $1/\gamma$, is much faster than the dynamics in the system. This approximation leads to various quantum master equations, including the Redfield formalism.

The approximation clearly breaks down for systems where the environment evolves on a time scale similar to the system. In the extreme case, where the time scale of the environment is much slower than any system dynamics, the bath is essentially frozen. This leads to a nonergodic situation, in which each system in the ensemble interacts with a different, static environment. Dissipation is absent in this limit. Here, we use the hierarchy of equations of motion approach to study the situation in which the system and environment time scales are similar. This is typically the case in exciton transport in biological systems, as well as for qubits in a complex environment. In this case, the correct exciton dynamics is significantly different from the Markovian prediction. Furthermore, depending on the excitation mechanism, initial correlations between system and environment can be important.
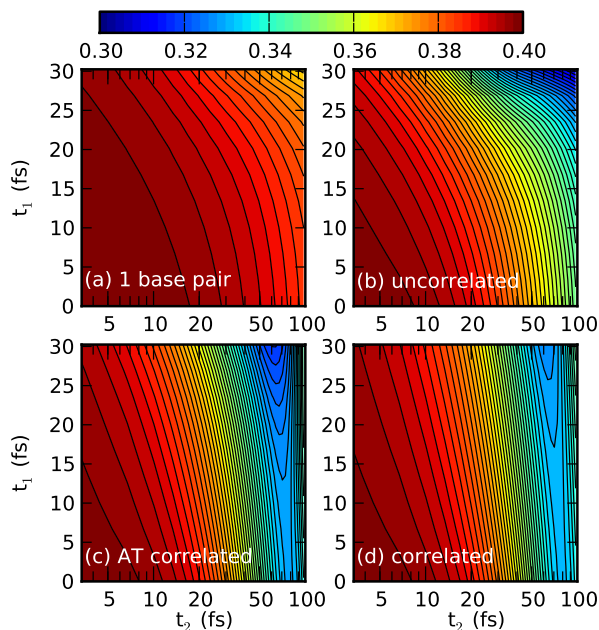

FIG. 2. Two-time anisotropy decay in a B-DNA helix for (a) a single base pair and 12 bases with (b) uncorrelated fluctuations in each base, (c,d) correlated fluctuations (from Ref. 4).

Unlike in the Markovian case, where these correlations decay directly, they influence the exciton dynamics after excitation. To show the effect of initial correlations, we plot the entanglement of two qubits after excitation in Figure 1. It is clear that there is a significant difference between the predictions of the Redfield theory and the exact results, originating in the time scale of the environment. As a second example, we show a nonlinear optical observable - the two-time anisotropy decay - in Figure 2. Comparing such calculations with experiment can shine light on the exciton dynamics.

Conclusion In conclusion, we have studied excitons in a complex environment, in the case where the exciton dynamics occurs on a similar time scale as the motion of the environment. In this case, approximations such as the Markovian limit, or a static environment, break down. In future work, it will be of interest to extend the calculations to other observables, such as the various two-dimensional spectra, as well as to other physical systems.

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