A phenomenological description of the bath and its effect in photosynthetic light-harvesting systems

JA Nöthling[1], **TPJ Krüger**[1] **and T Mančal**[2]

[1] Department of Physics, University of Pretoria, Lynnwood Road, Hatfield 0028, South Africa
[2] Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5 CZ-12116, Czech Republic

E-mail: `janothling@gmail.com`

Abstract. It is practically impossible to calculate the dynamics of each degree of freedom in a large, complex quantum system. When only a small part of the system is of interest, the rest of the system can be modelled as a thermal bath consisting of an infinite number of independent harmonic oscillators. In quantum master equations, dynamics of the bath and the coupling of the relevant subsystem to the bath are introduced through bath correlation functions. However, the physical significance of these correlation functions and the microscopic dynamics and interactions of the bath, are not clear from the derivation of the master equations. In this paper we give a microscopic interpretation of the bath and discuss the significance of the correlation functions in the context of photosynthetic light harvesting. The ideas and results are applicable to many other quantum systems as well.

1. Introduction

In many fields of physics and chemistry, the dynamics of a small quantum subsystem contained in a much bigger system need to be calculated. The total system evolves unitarily and, in principle, its dynamics can be calculated exactly. In reality, these systems are far too big and far too complex to allow calculation of the dynamics of all degrees of freedom. Since the dynamics of the subsystem depends on interaction with the rest of the system, considering an isolated subsystem is also not a solution. In general, due to energy exchange between the subsystem and the other degrees of freedom, it is not even possible to describe the subsystem dynamics with a Hamiltonian approach. One of the ways to treat this problem is to partition the total Hamiltonian in three parts [1]: H_S describing the subsystem as if it were an isolated system, H_B describing the rest of the system (bath) as if it were isolated and H_{SB} describing the interaction between the relevant subsystem and the bath. Instead of treating H_B and H_{SB} exactly, the actual bath is substituted with an effective bath having more or less the same effect on the system. A commonly used effective bath consists of an infinite number of independent quantum harmonic oscillators [2]. These harmonic oscillators are coupled linearly (see below) to the relevant subsystem. The harmonic bath causes both fluctuations and dissipation in the relevant subsystem. Although this approach is useful for many physical systems, its application to photosynthetic light harvesting will be discussed to emphasize its applicability.

2. A brief introduction to quantum dynamics in photosynthesis

Photosynthesis can be summarised as a process consisting of two phases. In the first phase, light energy is captured and transported to a photosynthetic reaction center [3]. The second phase, which is initiated at the reaction center, entails the conversion of the captured energy to energy-rich chemical compounds [4]. The capturing and energy conversion phases can be regarded as separate processes. The light-harvesting complexes responsible for capturing light energy consist of pigment molecules embedded in a protein conglomerate [5]. During the light capturing phase, a photon is absorbed and its energy used to excite a pigment molecule from the ground state to an electronic excited state. This excitation is transferred from pigment molecule to pigment molecule until it reaches the photosynthetic reaction center from where the chemical conversion phase is initiated [3]. The quantum efficiency of the first phase is extremely high; often more than 95% [6]! This high efficiency was one of the catalysts for the large interest in theoretical biophysics in recent years. Most of this research field is focused on the quantum mechanical description of energy transfer during the energy-capturing phase of photosynthesis. The light harvesting complexes are very large and intricate macromolecules (see for example [7]). To describe the dynamics of all the degrees of freedom is impossible. In general, we are interested only in the electronic degrees of freedom. However, the protein scaffold is important for energy quenching and its effect on the electronic degrees of freedom has to be considered. For these three reasons the Hamiltonian-partitioning approach outlined above is frequently used.

3. The relevant system[1]

Each of the pigment molecules in a light harvesting complex can be regarded as a two-level system with a ground state and an excited state [8]. Due to the possibility of excitation, each pigment molecule has an associated transition dipole moment. The transition dipole moments of different molecules interact in a similar manner as transient dipole moments in matter do to bring about London dispersion forces. One can say that different pigment molecules are *coupled* to one another. The strength of the coupling depends on the distance and relative orientations of the pigment molecules. The Hamiltonian of the relevant system is therefore:

$$H_S = E_g \left|g\right\rangle \left\langle g\right| + \sum_{i=1}^{N} E_{e_i} \left|e_i\right\rangle \left\langle e_i\right| + \sum_{i \neq j}^{N} V_{ij} \left|e_i\right\rangle \left\langle e_j\right|, \tag{1}$$

where the first term is the ground state energy of the system (all pigment molecules are in their ground states) and the second term is a sum of single-excitation energies (only molecule i is in the excited state). The last term represents the dipole coupling between different pigment molecules.

In what follows, we will mostly consider a single pigment molecule as the relevant system. Extension to more than one pigment molecule does not change the way in which the bath couples to the relevant system.

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[1] The word ”system” can cause confusion. We will use the term ”relevant system” for the electronic degrees of freedom and ”bath” for all other degrees of freedom such that the union of relevant system and bath evolves unitarily in time. We will reserve the term ”system” exclusively for this union.

4. Interaction of the relevant system with an oscillator

Consider an isolated pigment molecule consisting of two identical subunits. For comparison with Eq. (1), we will call this molecule i.

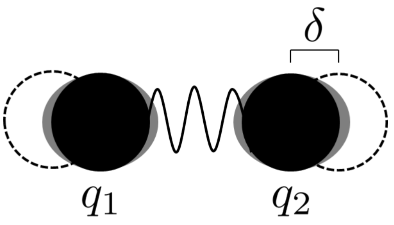

Figure 1. A pigment molecule consisting of two identical subunits. The coordinates of the two subunits measured on the same coordinate axis are given by q_1 and q_2, and δ is the equilibrium shift in each of these coordinates upon excitation of the molecule.

One of the vibrational modes of the molecule constitutes stretching and contracting along the axis connecting the two subunits. Let's consider an effective coordinate $Q = q_1 - q_2$. The potential energy causing the oscillation is now quadratically dependent on Q. Let the minimum of this potential be indicated by the black circles when the molecule is in its ground state. Suppose that the structure of this molecule in its excited state is such that the equilibrium position of each subunit is shifted a distance δ outwards. The potential minimum (in coordinate Q) is therefore shifted by $d = 2\delta$. Because of the large masses of the subunits, one can assume that the oscillations happen on a much slower timescale than the transition from the ground to the excited state in molecule i (adiabatic approximation). To excite molecule i from the vibrational ground level of its electronic ground state, one therefore has to apply more excitation energy than the energy difference $E_{e_i} - E_g$ in Eq. (1). The energetics accompanying the electronic excitation is depicted in figure 2. The parameter d in figure 2, which is equal to 2δ in figure 1, describes how strongly the relevant system is perturbed by (or *coupled* to) the oscillation. This parameter will be useful later again.

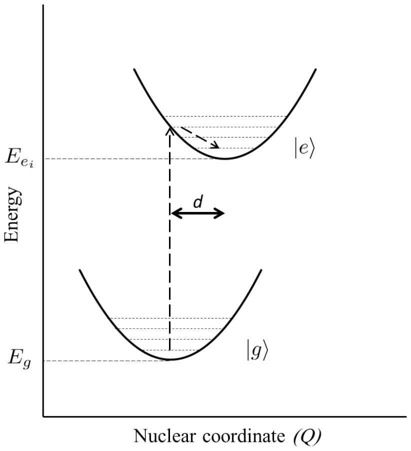

Figure 2. The harmonic oscillator potentials corresponding to the ground and excited states of a pigment molecule with two subunits. E_g and E_{e_i} are the energies of the ground and excited electronic states respectively. As indicated by the dotted line arrows, the molecule is excited to a non-ground vibrational level of the electronic excited state, before relaxing to the ground vibrational level. The parameter d is an indication of the coupling strength between electronic excitation and the molecular vibration.

Although it is very elucidating, the discussed model is an oversimplification: the pigment molecules are complex structures and have numerous intramolecular vibrational modes. In addition, intermolecular vibrations due to other pigments and the protein environment need to be taken into account. One can think of these protein vibrations as damping or driving oscillations of pigment molecules. To account for all of these vibrations, one can consider the system as an electronic two-level system coupled to a collection of normal harmonic oscillator modes called the bath.

5. The bath

In general, microscopic knowledge of the system is not necessary. It is not necessary, for example, to know the exact positions or configurations of proteins in photosynthetic light harvesting complexes. We can replace the real bath with an infinite set of harmonic oscillators as long as the interaction with the relevant system is the same for the original and the new bath. The Hamiltonian of the system is then

$$H = |g\rangle H_g \langle g| + |e_i\rangle H_e \langle e_i|, \tag{2}$$

with

$$\begin{aligned} H_g &= \sum_l \big[\frac{p_l^2}{2m_l} + \frac{1}{2}m_l\omega_l^2 q_l^2\big] \\ H_e &= \hbar(E_{e_i} - E_g) + \sum_l \big[\frac{p_l^2}{2m_l} + \frac{1}{2}m_l\omega_l^2 (q_l - d_l)^2\big], \end{aligned}$$

where m_l, q_l, p_l and ω_l are the mass, coordinate, momentum and frequency of the l^{th} oscillator and d_l is the distance by which the coordinate equilibrium of oscillator l is shifted upon electronic excitation of the pigment molecule.

Instead of coupling only to a single harmonic oscillator like in figure 2, the relevant system now couples to infinitely many independent harmonic oscillators. This model is known in literature as the Spin-Boson Model [2].

While it is clear from Eq. (2) how the bath is changed when the relevant system is excited, the opposite effect (change of the relevant system due to the bath) is not clear. In Markovian master equations based on the Spin-Boson Hamiltonian, the bath degrees of freedom enter the equation of motion only through two-times correlation functions of the form $C(t) = \langle q_n(t)q_n(0)\rangle$, where q_n is the bath coordinate coupled to the n^{th} pigment molecule and $\langle\ldots\rangle$ indicates ensemble averaging over the bath degrees of freedom. If one does not have any knowledge of the microscopic nature of the bath, it is hard to give a physical interpretation of these correlation functions from the derivation of the quantum master equations.

An equivalent way of thinking about the Spin-Boson Model is the so-called Multimode Brownian Oscillator model [2] (which one can consider as an extended Jaynes-Cummings model). In this model the relevant system is linearly coupled to a finite set of harmonic oscillators, like in Eq. (2). In turn, these harmonic oscillators (which we will call the primary oscillators) are coupled linearly to an infinite set of other harmonic oscillators (which we will call the free oscillators since they are not coupled to the relevant system). A schematic of this model is shown in figure 3. It is important to note that the bath correlation functions enter the master equation description through commutators of the relevant system-bath interaction Hamiltonian. Since the free oscillator coordinates don't appear in this interaction Hamiltonian, the only correlation functions in the master equations are therefore the ones containing the coordinates of the primary oscillators. These correlation functions are statistical parameters comparing the coordinates of the primary harmonic oscillators at two different times. These parameters are determined by the coupling of the primary oscillators to the free bath and the relevant system.

6. Effect of the bath on the relevant system

The bath provides both fluctuations and dissipation in accordance with the Fluctuation-dissipation theorem [1]. The primary oscillators are quantum Brownian oscillators (quantum

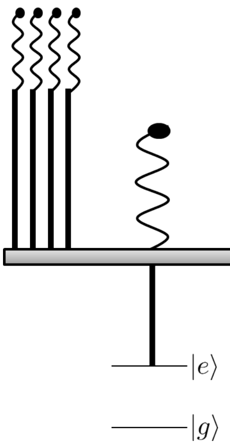

Figure 3. A schematic of the quantum Multimode Brownian Oscillator model. The straight vertical lines indicate linear coupling and the grey bar represents the primary oscillator.

oscillators subject to the fluctuating net force of an infinite set of other oscillators). The thermal fluctuations of the free oscillators cause the primary oscillator coordinates to fluctuate. Through the linear coupling between the primary oscillator coordinates and the relevant system, the excited state energy (and therefore the energy gap between the ground and excited state) of the pigment molecule also fluctuates. When the fluctuating energy gap of one two-level system corresponds to the energy gap of another two-level system, resonance energy transfer between the two-level systems is induced. In this way the bath facilitates energy transfer between pigment molecules.

The bath also acts as dissipator. When energy is transferred from one pigment molecule to a non-ground vibrational level of another pigment, the bath can dissipate the energy difference between the latter vibrational level and the ground level through the coupling to the free bath. Because the free bath has so many degrees of freedom, the energy is never transferred back to the system. This dissipation continues until the system as a whole reaches thermal equilibrium.

In order to show how the effect of bath fluctuation and dissipation on the relevant system can be characterised, let's suppose that, as shown in figure 3, we describe the system with only a single primary oscillator. This single oscillator is the link between the free bath and the relevant system, and the effect of these two subsystems on each other should therefore be channelled through the primary oscillator. All the dynamics of the bath which have an influence on the system can be therefore be obtained by a characterization of the primary oscillator coordinate. The bath correlation functions provide such a characterisation.

To get a better understanding of the meaning of these correlation functions, let us consider a specific correlation function; that of an overdamped Brownian oscillator [2]. This correlation function is often used in simulations because it can be calculated analytically and depends on only three physical parameters: the temperature, bath decorrelation time and the bath reorganisation energy (the energy released when the system relaxes to a ground vibrational state—see figure 2). This correlation function is a complex number for a quantum oscillator. As a very crude approximation, however, one can assume this correlation function (for each pigment molecule) to be an exponentially decreasing function like it is in the classical case. Let us now expand our relevant system to a number of pigment molecules with varying coupling between them. It was noted earlier that $\langle \ldots \rangle$ indicates an ensemble average. Suppose therefore that we prepare a very large number of initially identical systems and measure the product $q_n(t)q_n(0)$ in each of them. The correlation function $C(t) = \langle q_n(t)q_n(0)\rangle$ will then be an average of all those measurements. Assuming the crude approximation for the correlation function discussed above, the ensemble average of $C(t)$ will be non-zero immediately after electronic excitation of the i^{th} pigment molecule in the system. This means that all systems (and relevant systems) in the ensemble behave similarly and the dynamics of the relevant system (which is also determined by an ensemble average) are driven in a specific direction by the bath. When the correlation functions decayed significantly, different members of the ensemble behave differently and there exist no net drive on the system due to the bath. It is clear now that the bath correlation functions can be thought of as parameters determining the strength and duration of the influence of the bath on the system.

7. Conlusion

We have described how a complex quantum system can be partitioned into a small relevant subsystem and a bath. The Spin-Boson Model was introduced to describe the bath and the interaction of the relevant system with the bath. The effects of the bath (fluctuation and energy dissipation) on the relevant system were illustrated by considering the Multimode Brownian Oscillator model, which is equivalent to the Spin-Boson Model. The statistical importance and the physical interpretation of the bath correlation functions were discussed. The correlation functions characterises the strength and duration of the bath's influence on the relevant system.

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