22nd Solvay Conference in Chemistry

Quantum dynamics of bio-molecular systems in noisy environments

S.F. Huelga[a], M.B. Plenio[a,b]

^{a}*Institut für Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany*
^{b}*Quantum Optics and Laser Science group, Blackett Laboratory, Imperial College London, London SW7 2BW, UK*

Abstract

We discuss three different aspects of the quantum dynamics of bio-molecular systems and more generally complex networks in the presence of strongly coupled environments. Firstly, we make a case for the systematic study of fundamental structural elements underlying the quantum dynamics of these systems, identify such elements and explore the resulting interplay of quantum dynamics and environmental decoherence. Secondly, we critically examine some existing approaches to the numerical description of system-environment interaction in the non-perturbative regime and present a promising new method that can overcome some limitations of existing methods. Thirdly, we present an approach towards deciding and quantifying the non-classicality of the action of the environment and the observed system-dynamics. We stress the relevance of these tools for strengthening the interplay between theoretical and experimental research in this field.

Keywords: Quantum dynamics, networks, noise, bio-molecular, coherence, entanglement, non-classicality

1. Introduction

At the fundamental level Nature is quantum mechanical and it is therefore not surprising that quantum coherence and entanglement exist in well isolated multi-component systems, such as the electrons involved in chemical bonds. One may argue, however, that in such situations, when the system is static, coherence and entanglement can always be made to vanish in a suitably chosen basis unless there is a natural (spatial) separation into distinguished subsystems. Hence, to observe non-trivial quantum effects we need to force the system out of its eigenbasis, through intervention from the outside, and thus probe quantum coherences between eigenstates as well as the quantum coherence properties of their consequent dynamics. It is therefore the dynamics generated by the external perturbation that results in relevant quantum phenomena and provides the means to probe for interesting quantum properties. The external perturbation may either be coherent and controlled, as it would be favoured by an experimentalist aiming to interrogate the system, or it may be provided by an interaction with an unobserved environment. The latter will always be present, as it is never possible to completely isolate a physical system from its environment. In fact, in bio-molecular systems the interaction with uncontrolled environments, for example in the form of thermal fluctuations, is an important driving force of its dynamics and hence its functionality. It may therefore be expected that the interplay between the internal coherent quantum dynamics of the system and the unavoidable presence of noise introduced by the environment has been optimized by Nature and may be significant for its function. In fact, despite the tendency for environmental noise to destroy coherence through the introduction of classical randomness, it is also well known to have the capacity to lead to the generation of coherence and entanglement and be instrumental for its persistence in the steady state [1, 2]. It is then an interesting question to determine up to what extent are quantum dynamics, coherence and entanglement present in composite quantum systems in contact with environments, such as bio-molecular systems and, importantly, what role,

if any, genuine quantum traits may play for its functionality. These questions become particularly challenging in bio-molecular systems where the strength of the system-environment interaction is often comparable to the intra-system coherent coupling strengths. This non-perturbative regime is most challenging, as it sits uncomfortably between the two standard limiting cases in the system-environment interaction that admit relatively straightforward treatments. Hence novel theoretical methods will need to be developed, a task that may benefit from the increased understanding of quantum dynamics of composite quantum systems that has emerged in recent years in quantum information science.

A variety of challenges present themselves. Firstly, composite quantum systems or quantum networks in noisy environments will exhibit a wealth of dynamical features whose complexity will increase very rapidly, perhaps even exponentially, with the number of components thanks to the concomitant growth of the size of the state space. One approach may simply consist in the development of increasingly detailed models that reproduce the dynamics with the help of a sufficient number of free parameters. While this may be suitable for smaller systems, it rapidly becomes neither workable nor fruitful for larger ones - a situation not dissimilar from that encountered in entanglement theory in quantum information science [3]. However, knowing all the details, i.e. knowing all the parameters determining the dynamics, does not necessarily lead to greater understanding. More might be learnt if one distils key elements that govern the dynamics and that are broadly applicable across a large number of systems. In the context of noise assisted transport, steps towards this goal have been taken and will be outlined briefly.

Secondly, even if it is possible to deduce some of these key principles on the basis of simplified models for the system environment interaction, it will become necessary to put these principles to the test in increasingly realistic models of the system-environment interactions and, crucially, in actual experiments. This challenges current methodology which has been derived largely for the limiting case of weak or strong system-environment coupling. Hence new tools need to be developed for the intermediate regime admitting increasingly precise descriptions together with, ideally rigorous, error bounds to enable the reliable benchmarking with respect to each other. In this note we will briefly discuss existing methods, pointing out strengths and weaknesses and outline a novel approach that is bringing together methods from mathematics, condensed matter physics and quantum information and holds the promise of overcoming some of the limitations of existing methods.

Thirdly, the experimental and theoretical study of the dynamics of multi-component systems in the presence of noisy environments raises the question of assessing at what point the system and its dynamics may be considered quantum coherent and at what point the system dynamics has become classical, in a quantitative fashion. The very same questions may be raised concerning the action of the environment acting on the system. In fact, judging reliably when it is really necessary to model the environment quantum mechanically and providing a classification of those physical quantities for which an accurate specification can be achieved by modelling the environment in terms of a fluctuating, possibly non-Markovian, classical field could lead to considerable simplifications in the description of quantum dynamics in bio-molecular systems. Furthermore, robust and well-founded methods for the quantification of the quantum character of bio-molecular dynamics would provide conceptual tools to deliver "extraordinary evidence for extraordinary claims" of the existence of quantum coherence as required in [4]. Quantum information theory has longed grappled with the quantification of quantum resources and we will discuss these questions briefly bringing to bear methods from this discipline.

2. Structural elements of noise assisted quantum dynamics

Exciton energy transfer (EET) has been actively studied within the chemical physics community for decades [5, 6, 7, 8, 9, 10], yet the topic remains timely [11, 12, 13], mainly due to the development of new spectroscopic techniques in the femtosecond time scale. Ultrafast nonlinear spectroscopy has been used recently to probe energy transfer dynamics in the Fenna-Matthew-Olson (FMO) and other photosynthetic aggregates [14, 15, 16, 17, 18]. The FMO complex is an example of a pigment-protein complex (PPC), a network through which electronic excitations on individual pigments can migrate via excitonic couplings. These experiments have provided evidence for the existence of significant quantum coherences between multiple pigments through the presence of wave-like beating between excitons which has been observed to persist on timescales > 550fs, a significant fraction of the typical transport time in FMO. As a result, there is now considerable interest in exploring the possibility of assigning a functional role to quantum coherence in the remarkably efficient excitation energy transfer in FMO and other PPCs. Theoretical investigations of the role of pure dephasing noise in EET have found that this noise mechanism has the ability to enhance both the rate and yield of EET when compared to perfectly quantum coherent evolution [19, 20]. In the exciton

basis normally used in previous studies [21], dephasing-assisted transport (DAT) is considered to be resulting from noise-induced transitions between exciton eigenstates states, which cause energetic relaxation towards the reaction centre. This approach suffices to suggest the existence of EET as a noise-assisted processes but it is less transparent in showing how DAT actually works, when it does not exist or is inefficient and how it might be controlled or exploited in artificial nanostructures. Here we would like to provide a fresh look at the problem by aiming at clearly identifying the mechanisms that are underlying noise assisted transport [19, 20, 22, 23, 24, 25, 26, 27]. Identifying and spelling out these mechanisms clearly does provide additional value even if the individual contributions might have been known in some context. Such classifications pave the way towards tailored experimental tests of individual contributions [28] while the clear understanding of these fundamental mechanisms will allow for the optimization of network architectures in order to utilize quantum coherence and noise optimally in artificial nanostructures. Here we briefly outline the developments of [20, 23, 24, 26].

2.1. Description of elements

The fact that noise can assist transport is well known in certain contexts. For instance, incoherent hopping between neighbouring molecules can be facilitated by the line broadening resulting from a variety of processes. It is also well established that interference effects in infinitely extended quantum networks can preclude transport, as strikingly illustrated by the phenomenon of Anderson localization in large lattices. We will summarize in this section recent results showing that environmental noise can also assist the excitation transport across finite networks and will identify the underlying basic mechanisms for DAT which are also relevant for more general noise processes. With this background, we will discuss a simple model of transport across the Fenna-Matthew-Olsen (FMO)-complex, a bio-molecular wire present in types of photosynthetic bacteria, and show that it's near unit transport efficiency can be understood as the result of a dephasing assisted process. For clarity and simplicity let us begin by considering a network of N sites such as the one illustrated in Figure 1 even though the considerations are general [23]. Each site is modeled as a two level system corresponding to having either none or one excitation at the corresponding site. Local sites couple to each other via a coherent exchange interaction. When each site couples to any other in the network with equal strength, the network is said to be fully connected. The question we focus on is the following: If site 1 is initially excited, what is the probability that at a subsequent given time t the excitation has been transferred to a sink to which a selected node s is irreversibly coupled? It can be shown that transport across this type of network is
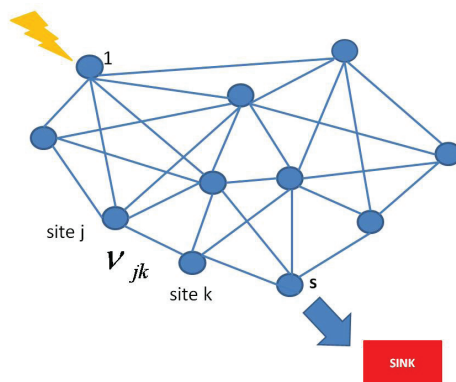

Figure 1: Quantum network of arbitrary geometry. Network sites are modeled as two level systems and excitations can propagate across the network via coherent exchange interactions. Select sites labelled 1 and s receive an initial excitation and are irreversibly coupled to a sink respectively. Quantum effects may significantly inhibit transport, so that in the limit of large number of sites N, no population is transferred to the sink. Environmental noise in the form of pure dephasing can significantly alter this pattern and assist efficient population transfer

highly inefficient and that the asymptotic sink population scales inversely with the number of sites so that transport is essentially inhibited already for a moderate size network [23]. The fundamental reason behind this is the exact cancelation of tunneling amplitudes of delocalized anti-symmetric states. It is remarkable that thanks to the initialization of the excitation in a single site, the network will generally have a high probability to evolve into a trapped state irrespective of the detailed network structure. The coherent evolution of the network therefore leads to the emergence

of trapping states and precludes excitation transfer to the sink, while purely incoherent hopping across the network would eventually lead to complete transfer. It is now apparent that the transport can become noise-assisted if a type of noise is provided that is able to disturb the formation of invariant subspaces, which are decoupled from the sink. This is precisely what local dephasing, and other forms of noise, can do. As opposed to relaxation, dephasing noise leaves the site population unchanged but destroys the phase coherence of superposition states. When subject to dephasing noise, cancelation of tunneling amplitudes is no longer exact and the condition for excitation trapping is removed. Dephasing noise is therefore able to open up transport paths that interference effects had rendered forbidden and facilitate the transfer to the sink. The transfer efficiency becomes a non-monotonic function of the local dephasing rates [19, 20, 22, 23, 24, 25] so that an optimal noise strength can be found for which transport is most efficient and at which quantum coherence is partially but not completely suppressed [26]. Higher levels of noise lead to the effective localization of the excitation and therefore transport is again compromised. It should be noted that the decohering effect of strong noise may also be used constructively in blocking undesirable paths for propagation in the system by selectively applying noise to specific sites.

There are a number of additional building blocks that contribute to the dynamics of such a quantum network. Destructive interference may also be obstructed by the presence of static disorder in the network as this leads to the development of time dependent relative phases at a rate proportional to the energy difference between sites. This in turn rotates the system out of trapped states into propagating states and hence aides transport. However, there are limits to the efficiency of this mechanism, as energy gaps that are larger than the coupling matrix elements will lead to suppression of transport due to energy conservation. Here noise may again play a constructive role as fluctuations of energy levels lead to line broadening and hence an enhanced overlap between lines. Alternatively, one may view this process dynamically and realize that, thanks to the fluctuations, energy levels sometimes become near degenerate and hence permit transport. Excessive fluctuations however will lead to small time intervals in which levels are near degenerate and hence transport will reduce again leading to a non-monotonic behaviour of the excitation transfer as a function of the noise strength. It should be noted that also quantum coherent interactions generally shift and split energy levels. This can provide functional advantages as it may lead to a broader absorption spectrum (e.g. in the LHII system) and may, as we will see below, also move energy levels between which transfer is desirable closer to each other. On the other hand, it unavoidably also shifts energy levels further apart and hence noise may again be needed to bridge those gaps.
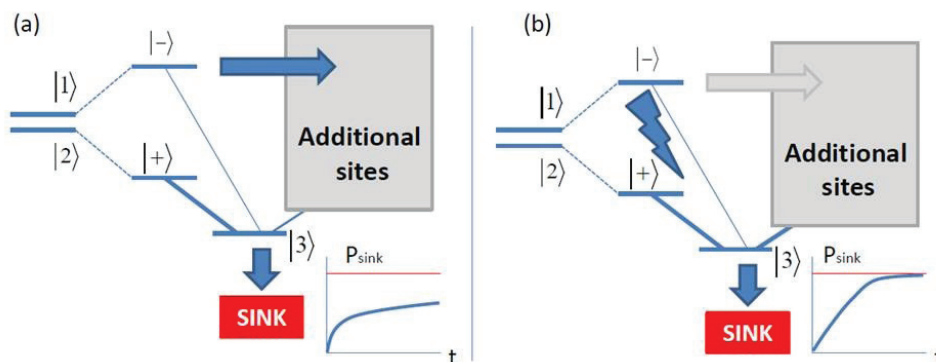

Figure 2: Noise-assisted energy transfer across FMO can be qualitatively understood by introducing a hybrid basis of local sites. While a purely unitary evolution yields to inefficient transport, as discussed in the text, the presence of dephasing noise eliminates inefficient transport paths while opening up new channels for excitation transfer. While the estimation for the transfer efficiency under coherent evolution is well below 100%, a simple noise model brings this number close to perfect efficiency within the observed transfer time.

We argue that these basic principles also apply for general networks. To illustrate how the general principles outlined above may feature in a more realistic scenario, we will consider briefly the example of excitation transfer across a monomer of the FMO complex, which can be modeled as a 7 sites network and for which detailed information concerning the system Hamiltonian is available [12]. Given the strong coupling of sites 1 and 2 these levels are shifted and mixed and the dynamics is conveniently described using an hybrid basis [24] for these two sites that we denote by $|\pm\rangle$. In this basis, the Hamiltonian has the local site energies and coupling structure shown in Figure 2, where site

3 is connected to a sink node that models the actual reaction center and all the remaining sites have been packed in a block (labeled as "additional sites" in Figure 2) that is uncoupled from the level $|+\rangle$.

When an excitation is injected in site 1, the coherent evolution leads to transfer efficiency P_{sink} below 60%, far from the ideal transfer, represented in Figure 2 by the red horizontal line. The coherent interaction between sites 1 and 2 leads to level splitting and moves one of these energetically closer to site 3 while the other is farther removed. Furthermore, interference of transition amplitudes from the states $|+\rangle$ and $|-\rangle$ will contribute to the dynamics as explained above. The introduction of local dephasing noise can dramatically alter this picture and lead to perfectly efficient transport to the sink, as illustrated in the part (b) of the Figure. Coherent oscillations between level $|-\rangle$ and the rest of the complex are now largely suppressed, while an incoherent transfer path between previously decoupled levels $|\pm\rangle$ is now active, leading to a fast transfer of population to the sink. Furthermore, destructive interference between propagation paths is reduced. Within this model, it is possible to optimize the local dephasing rates so as to reproduce the observed transfer rates in the correct time scale. More detailed discussions can be found in the literature [19, 20, 23, 24].

2.2. Remarks

There are two aspects that we should stress in order to conclude this section. The first one concerns the independence of the main results from the very specific details of the noise model; while initial work involved simple dynamical evolutions of the Lindblad form [19, 20], subsequent studies refined the noise model to also account for certain non-Markovian effects [24]. Secondly, the range of noise parameters leading to efficient transport is rather broad so that the interplay between coherent and noisy processes does not require a fine tuning, but is robust to variations in both the system Hamiltonian and the parameters characterizing the system-environment coupling. These results challenge the traditionally held view that noise tends to degrade the efficiency of quantum processes, and demonstrates that controllable noise can even be considered as an additional engineering tool for excitation transport [19, 20, 23, 24, 25, 26]. Needless to say, in addition to these theoretical calculations it should be crucial to provide a direct experimental test for the relevance of noise assisted transport as well as the basic mechanisms that underly the dynamics of the FMO complex. Here techniques from optimal control for state preparation may become crucial to realize recent proposals towards this goal [28].

3. Numerical simulation of noisy quantum dynamics

The previous section has demonstrated that the interaction between system and environment can be of crucial importance for both dynamics and functionality of the system. Furthermore, the optimal operating regime, at least with respect to transport, is found to be one in which the strength of the system-environment interaction, characterized by the so-called reorganization energy, is comparable to the intra-system coupling rates. This regime is quite different to the two extreme cases in the system environment interaction that are usually studied and which admit perturbative treatments. On the one hand, very strong coupling leads to a dynamics that is well approximated by classical rate equation models. Weak system environment coupling on the other hand permits a perturbative treatment in which environmental dephasing and relaxation can be treated with Lindblad or Bloch-Redfield master equations which are both based on the assumptions of weak system bath coupling and the Markov approximation. The intermediate regime, however, appears to be of particular relevance to bio-molecular systems but at the same time poses greater challenges as it is intrinsically non-perturbative. Here perturbative expansions that assume environments with correlation times that are much smaller than the system dynamics are not well justified. Indeed, in the limit of slow bath dynamics, perturbative treatments of the system environment coupling cannot be used even if the system-bath coupling is intrinsically weak. Hence, in the light of its importance the development of methods for the exact and flexible description of system-environment interaction in this regime is well motivated. In fact, the development of such methods has gathered pace and recently, a variety of steps have been taken towards the development of fully non-perturbative and non-markovian approaches. The relative merits of the different approaches have not been compared and contrasted yet, nor have the regimes in which they may be optimal been identified. This would be a timely issue as it appears likely that different approaches will be best suited for different physical settings and different quality measures and requirements.

In the following we discuss three of the approaches that are being pursued in the literature and suggest strengths and weaknesses of these methods.

3.1. The hierarchy method

Recently, the numerical hierarchy technique [29, 30, 31, 32], which has a longstanding history [33, 34, 35], has received renewed attention in the context of EET across pigment-protein complexes. This approach is non-perturbative and is capable of interpolating, for example, between the Bloch-Redfield and the Förster regimes [29, 30]. It derives a hierarchy of equations in which the reduced density operator of the system couples to auxiliary operators which in principle allow for the simulation of complex environments. The depth of this hierarchy and the structure of its coefficients depend on the correlation time of the bath and its spectral density. This approach appears sufficiently flexible to take account of spatial correlations in the noise as well. For specific choices of the bath spectral density, namely the Brownian harmonic oscillator, and some mild approximations, one obtains a relatively simple structure of the hierarchy. In this case, the temporal bath correlations decay exponentially so that the hierarchy can be terminated early with small error. An estimate suggests that in this case the set of operators in the hierarchy will scale at least with τ^k where τ is the correlation time and k is the number of sites in the system to be studied (see [27] for a more detailed discussion). More complex spectral densities will lead to considerably more demanding evaluations of the coefficients of the hierarchy. A non-exponential decay of the temporal bath correlations also leads one to estimate an exponential growth of the number of operators in the hierarchy. It is possible that specific numerical simulations turn out to be more efficient than those estimates suggest but there is no certificate that provides error bounds. In fact, it is a challenge to provide rigorous bounds of the errors introduced by the various approximation steps that are involved in the numerical hierarchy technique. Hence one has to test for convergence empirically by increasing the depth of the hierarchy until the result do not change significantly anymore. It should be noted, that the hierarchy method has been applied successfully to a dimer [29, 30] as well as the seven-site FMO complex [36] with a Brownian harmonic oscillator spectral density of the environment.

3.2. Path integral methods

A variety of other approaches to study transport processes and in consequence also transport in noisy environments have been developed in condensed matter physics. Recently some of these have been applied to dimer systems with the aim of understanding better the evolution of quantum coherences in structured environments. These methods represent various approaches for solving numerically the formal path integral solution of the time evolution. These include the quasi-adiabatic path integral approach [37, 38, 39, 40, 41] and the iterative summation of real-time path integrals [42] to name just two approaches. These procedures are expected to give good results in the high temperature limit and hence short correlation time of the environments. With decreasing temperatures the computational effort is growing rapidly and the $T = 0$ limit cannot be reached, while temperatures not too far below the typical system frequencies appear to be accessible [43]. For highly structured environments in which for example both narrow and broad features are combined these methods find challenges. In this case, sharply peaked modes can be added to the system and their damping is treated in the bath [44] but such an approach will be problematic for the treatment of quantum networks when addition of modes make the network itself too high-dimensional for numerical treatment. Path integral methods have been applied mostly to dimers (see e.g.[41]) and their scaling to larger systems, just as for the transformation approach to be discussed below, remains to be demonstrated.

3.3. The transformation technique

An alternative approach that has the potential to address some of the challenges that we have raised above has been proposed recently. It treats the spin-boson model by a combination of analytical transformation techniques (building and improving upon earlier related work [45, 46]) to make it amenable to simulation methods from condensed matter physics and quantum information theory [47, 48]. In the spin-boson model, each two-level system couples linearly to the coordinates of a separate environment consisting of a continuum of harmonic oscillators presented schematically in Figure 3.a for the situation of a dimer. This model represents a suitable starting point for the description of excitation transport in pigment-protein complexes and is capable of encompassing a wide variety of dynamic behavior including non-Markovian dynamics as the vast majority of environmental modes in a pigment-protein complex are to a very good approximation harmonic [49]. Numerical treatments of the spin-boson model can be loosely divided into methods in which the environmental degrees of freedom are eliminated in order to derive effective equations of motion for the two-level system, and those in which the complete many-body dynamics of the two-level system and the environment are considered. The transformation approach treats the full system environment dynamics. In a first step the configuration
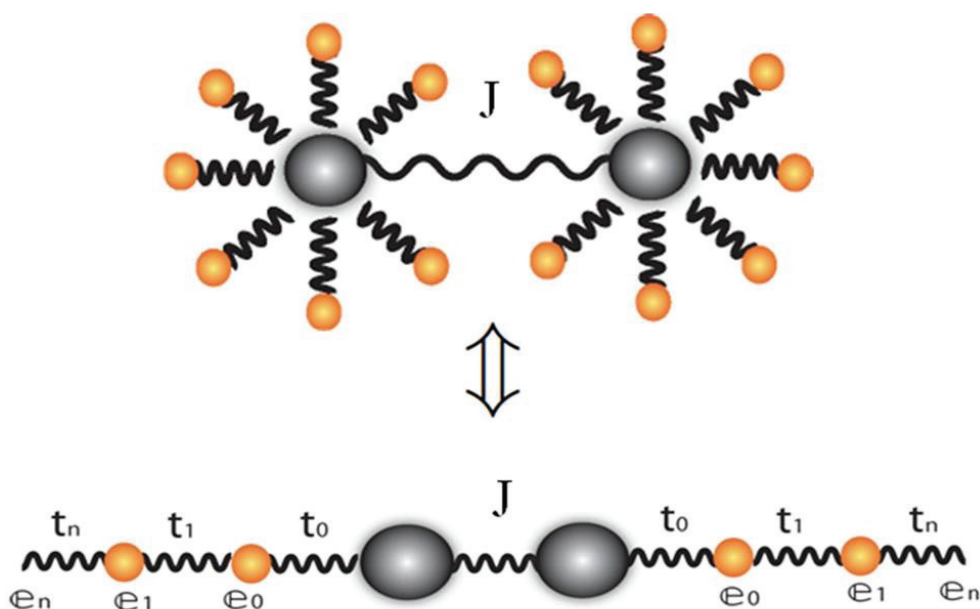
Figure 3: (a) Atop, in the standard representation of the spin-boson model considers central systems (grey spheres) coupled individually to a bath of bosonic modes representing harmonic oscillators. (b) Below, after an exact unitary transformation, solely affecting the bath degrees of freedom, the same number of bosonic modes are now arranged in a linear chain with nearest neighbour interactions only. The latter setting admits straightforward numerical description of the full dynamics with the time dependent density renormalization group method.

depicted in Figure 3.(a) is transformed into the linear configuration shown in Figure 3.(b) where each system site couples to a linear chain of bosonic modes with a nearest neighbor hopping Hamiltonian. This transformation, which can be determined analytically for a wide variety of spectral densities, or can otherwise be obtained in a numerically stable and efficient way, acts only on the environment degrees of freedom. As a consequence, the dynamics of the system, e.g. the pigment protein complex is unchanged. The dynamics of the resulting system + environment in Figure 3.(b) now has the appropriate structure (linear chain with nearest neighbor interactions) so that it can now be efficiently integrated numerically employing the time-dependent density matrix renormalization group algorithm [50]. The complexity scales linearly in the size of the environments.

This approach has several advantages. Firstly, the transformation approach works for arbitrary and possibly highly structured spectral densities of the environment without additional computational overhead. In particular, it is capable of including narrow features in general backgrounds and spectral densities leading to power law decay of the bath correlation function [47] without sacrificing its efficiency. Secondly, the time-dependent density matrix renormalization group algorithm and hence the transformation approach can be made arbitrarily precise (at the cost of what is usually a polynomial increase in computation time) and, crucially, delivers in each time step and hence also for the total evolution, an upper bound on the error committed. Hence the simulation delivers rigorous error bars from a single run. Finally, the transformation approach provides the full information about system and environment and their dynamics leading to a better understanding, for example, of the irreversibility of the system-environment interaction [48] but also opens the possibility of studying system-environment interactions in which the bath is prepared in non-trivial initial states or in which knowledge about the state of the environment should be extracted.

While the transformation method has been demonstrated for a dimer in contact with zero temperature environments, [47, 48] it is not restricted to this setting. It can be generalized to multi-site systems and finite temperatures at the expense of a moderate increase in computation time [51]. It should be noted however, that at present the inclusion of spatial quantum correlations between environments is challenging and restricted to simple cases. This may be a drawback for certain applications in which spatial correlations play a significant role but this does not appear to be the case in photosynthetic complexes like FMO. It should also be noted that the transformation approach immediately yields systematic approximation techniques (see also [52, 53]) by cutting short the chains that are obtained in the

exact transformation and coupling the last site to a Markovian bath [48].

3.4. Remarks

We have briefly outlined and discussed possible approaches for the numerical and analytical study of non-perturbativ system-environment interactions with a view to applying these methods to pigment-protein complexes. Each of these methods has been applied separately and certain strengths and potential weaknesses seem to emerge. However, as already mentioned before, a comprehensive comparison of all of these approaches has not been undertaken yet. Such a comparison would be highly desirable as it would allow us to ascertain the validity of the various approaches and also permit us to identify the most suitable methods for each possible experimental setting and for various success parameters. This would allow us to study a wide variety of questions of applied and fundamental nature. In particular, we may be able to consider the question to what extent the action of an environment is in fact quantum mechanical and what degree of approximation we can achieve with classical environment models. This and related questions will be discussed in the final section.

4. Assessing classical and quantum dynamics

Recent experiments are providing supporting evidence for the existence of quantum coherence and quantum coherent dynamics in a variety of bio-molecular systems despite the presence of strong coupling to the environment. The inferences concerning the quantum character drawn from these observations are however qualitative; the existence of oscillating features or off-diagonal elements in 2-D spectra serve as evidence that some quantum coherence is present or some quantum dynamics is taking place but does not make these statements quantitative. To pursue these questions in a more quantitative fashion it will be necessary to transfer tools from quantum information science that allow us to infer from the experimental data quantitative upper and especially lower bounds on the quantum mechanical properties of the system, ideally without invoking any experimentally untested assumptions. This might be done by studying entanglement measures [23, 26, 54, 55] but this approach suffers some drawbacks. Firstly, entanglement measures are often difficult to measure directly in actual experiments. Secondly, entanglement measures have been defined in quantum information science in a specific context, namely to study quantum information tasks in which we have a natural separation into subsystem (usually defined by distance) [3]. It is not clear that this approach is directly relevant to the study of quantum effects in biology. Here we would like to indicate briefly two aspects of this problem and possible ways forward that we are pursuing. Experimentally, we tend to be limited to snapshots of the dynamics at different times. On the basis of these observations we would like to quantitatively assess (a) whether the action of the environment can be modeled classically and if not, to what extent it deviates from being classical and (b) to what degree the dynamics of the system alone is quantum mechanical. Questions of this type have been posed before in quantum information science and we will be making use of the techniques developed there (see [56] for details).

4.1. Classical Environments

Ultimately, all dynamics needs to be described in the formalism of quantum mechanics and to make progress we define what is meant by a classical action of an environment in this framework. Intuitively, an environment should be termed classical if we can model it by a device that generates random numbers i with probability p_i and on the basis of these then applies a unitary action U_i to the system. Correlations between system and environment then remain classical at all times. Formally, if as observers we are ignorant of the value of i, such an action would result in the map of the system density operator $\rho \mapsto \Phi(\rho) = \sum_i p_i U_i \rho U_i^\dagger$. That is, the evolution can be expressed as a convex sum of random unitaries (a bistochastic map). Hence, if we measure experimentally for a certain time t the map Φ_t we can then determine whether this map can be written in the form $\sum_i p_i U_i \rho U_i^\dagger$ employing numerical methods [57]. If this is not possible, the action of the environment is non-classical. Remarkably, in the case that ρ represents a two-dimensional Hilbert space and the evolution is such that the identity is preserved (unitality condition), the resulting dynamics can always be expressed as a bistochastic map, while for any Hilbert space dimension larger than 2, exceptions exist. This does not however imply that the environment action on the system is classical if we perform more demanding experimental tests. After all, if we attempt to simulate the action of the environment, we need to do so not only mapping initial state into the final state but need to progress along a time sequence $t_0, t_1, \ldots, t_{fin}$. While at the initial time t_0 the system might be decorrelated from the environment, it will generally not be so at later times.

Then it is not evident anymore that the map Φ_{st} taking the system from time s to time t will also be classical, even if the maps Φ_t and Φ_s are classical separately. Hence, if we probe the system at times $t_0, t_1, \ldots, t_{fin}$ and determine the maps taking it from one time to the other and each of those maps is classical in the above sense then, for this time coarse graining, we would call the action of the environment on the system classical. This still leaves the question of the quantification of the degree of non-classicality of the environment action. As in the theory of entanglement, i.e. non-classical correlations, there may exist several possible quantifications. Taking an axiomatic approach one should define desirable properties of a measure of non-classicality of maps. The measure $C(\Phi)$ should vanish for maps of the form $\Phi(\rho) = \sum_i p_i U_i \rho U_i^\dagger$ which we have termed classical, it should also be such that for any Ψ the measure does not increase under composition with a classical map, i.e. for any $C(\Phi \circ \Psi) < C(\Psi)$. In analogy with the theory of entanglement, one may then define a measure $C(\Psi)$ as the distance of the map Ψ to the set of all classical maps [58]. The distance between maps is not uniquely defined but a suitable choice might be the relative entropy distance between the Choi-Jamiolkowski states [3] associated with these maps. Once such a measure is defined, it can also be used to obtain lower bounds on the non-classicality of maps by identifying the least non-classical maps compatible with the known parameters, quite in the spirit of related work in entanglement theory [59, 60, 61].

4.2. Classical System Dynamics

Needless to say, a classical action of the environment does not imply that the system dynamics itself is classical. In fact, the most classical setting is an environment that is decoupled from the system which allows the system to evolve coherently. Questions of this type are of relevance in quantum information where for example the quantum character of a memory needs to be assessed on the basis of a number of preparations and subsequent measurements [62, 63] and the question whether a dynamics exhibits quantum coherence or not may then be approached with similar tools. Let us start again by probing the dynamics of the system at one particular moment in time, t. We would like to designate a map classical if it can be replicated by a device that measures the system state initially and then produces a new state from the measured data only. This so-called measure and prepare procedure is of the form $\Phi(\rho) = \sum_i tr[\rho M_i]\sigma_i$ with positive linear operators M_i satisfying $\sum_i M_i = 1$. It will not be able to perfectly reproduce any possible map that can be realized in quantum mechanics as it necessarily introduces some noise in the system due to the indistinguishability of non-orthogonal quantum states. Again, the quantification of the non-classicality of the map can be achieved by employing measures derived via an axiomatic approach. The measure $C(\Phi)$ should vanish for maps of the form $\Phi(\rho) = \sum_i tr[\rho M_i]\sigma_i$, it should also be such that for any Ψ the measure does not increase under composition with a map of the form $\Phi(\rho) = \sum_i tr[\rho M_i]\sigma_i$, i.e. for any $C(\Phi \circ \Psi) < C(\Psi)$ and the measure is then defined as the distance between the map and the closest map of the form $\Phi(\rho) = \sum_i tr[\rho M_i]\sigma_i$. Probing the system at multiple times $t_0, t_1, \ldots, t_{fin}$ may be treated straightforwardly in this setting too. It is useful to know that the determination of maps of this type is closely related to problems of convex optimization whose methods can be made use of here [56].

5. Conclusions

Recent experimental results providing evidence of coherent behavior in EET across bio-molecular complexes have open up a most interesting path for multidisciplinary research. Subsequent theoretical work has clarified the importance of the interplay between environmental noise and the underlying quantum dynamics in these systems. However, the fundamental question of quantitatively linking quantum behavior and biological function remains open. In our view, developing novel techniques for optimally probing complex interacting quantum systems and efficiently processing the resulting experimental data will be crucial for finally discerning whether or not do quantum effects play a fundamental role in the dynamics of biological systems.

6. Acknowledgements

7. References

[1]   M.B. Plenio and S.F. Huelga, Phys. Rev. Lett. 88 (2002) 197901.
[2]   L. Hartmann, W. Dür and H.J. Briegel, Phys. Rev. A 74 (2006) 052304.
[3]   M.B. Plenio and S. Virmani, Quant. Inf. Comp. 7 (2007) 1.
[4]   P.G. Wolynes, PNAS 106 (2009) 17247.
[5]   T. Förster, Ann. Phys. (Leipzig) 2 (1948) 55.
[6]   A.G. Redfield, Adv. Magn. Reson. 1 (1965) 1.
[7]   M. Grover and R.J. Silbey, J. Chem. Phys. 54 (1971) 4843.
[8]   R.M. Pearlstein, J. Chem. Phys. 56 (1972) 2431.
[9]   H. Haken and G. Strobl , Z. Phys. 262 (1973) 135.
[10] V.M. Kenkre and R.S. Knox, Phys. Rev. Lett. 33 (1974) 803.
[11] G.D. Scholes, Annu. Rev. Phys. Chem. 54 (2003) 57.
[12] J. Adolphs and T. Renger, Biophys. J. 91 (2006) 2778.
[13] Y.C. Cheng and G.R. Fleming, Annu. Rev. Phys. Chem. 60 (2009) 241.
[14] T. Brixner, J. Stenger, H.M. Vaswani, M. Cho, R.E. Blankenship and G.R. Fleming, Nature 434 (2005) 625.
[15] G.S. Engel, T.R. Calhoun, E.L. Read, T.K. Ahn, T. Mancal, Y.C. Cheng, et al, Nature 446 (2007) 782.
[16] H. Lee, Y.C. Cheng, G.R. Fleming, Science 316 (2007) 1462.
[17] G. Panitchayangkoon, D. Haynes, K.A. Fransted, J.R. Caram, E. Harel, J.Z. Wen et al, PNAS 107 (2010) 12766.
[18] I.P. Mercer, Y.C. El-Taha, N. Kajumba, J.P. Marangos, J.W. Tisch, M. Gabrielsen et al, Phys. Rev. Lett. 102 (2009) 319007.
[19] M. Mohseni, P. Rebentrost, S. Lloyd and A. Aspuru-Guzik, J. Chem. Phys. 129 (2008) 174106.
[20] M.B. Plenio and S.F. Huelga, New J. Phys. 10 (2008) 113019.
[21] M. Cho, H.M. Vaswami, T. Brixner, J. Stenger and G.R. Fleming, J. Phys. Chem. B 109 (2005) 10542.
[22] A. Olaya-Castro, C.F. Lee, F. Fassioli Olsen and N.F. Johnson, Phys. Rev. B 78 (2008) 085115.
[23] F. Caruso, A.W. Chin, A. Datta, S.F. Huelga and M.B. Plenio, J. Chem. Phys. 131 (2009) 105106.
[24] A.W. Chin, A. Datta, F. Caruso, S.F. Huelga and M.B. Plenio, New J. Phys. 12 (2010) 065002.
[25] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, A. Aspuru-Guzik, New J. Phys. 11 (2009) 033003.
[26] F. Caruso, A.W. Chin, A. Datta, S.F. Huelga and M.B. Plenio, Phys. Rev. A 81 (2010) 062346.
[27] A. Ishizaki, T.R. Calhoun, G.S. Schlau-Cohen and G.R. Fleming, Phys. Chem. Chem. Phys. 12 (2010) 7319.
[28] F. Caruso, S. Montangero, T. Calarco, S.F. Huelga and M.B. Plenio, arXiv:1103.0929.
[29] A. Ishizaki and G. R. Fleming, J. Chem. Phys. 130 (2009) 234110.
[30] A. Ishizaki and G.R. Fleming, J. Chem. Phys. 130 (2009) 234111.
[31] A. Ishizaki and Y. Tanimura, J. Phys. Soc. Jpn. 74 (2005) 3131.
[32] A.G. Dijkstra and Y. Tanimura, Phys. Rev. Lett. 104 (2010) 250401.
[33] T. Takagahara, E. Hanamura, and R. Kubo, J. Phys. Soc. Jpn. 43 (1977) 811.
[34] Y. Tanimura and R. Kubo, J. Phys. Soc. Jpn. 58 (1989) 101.
[35] Y. Tanimura, J. Phys. Soc. Jpn. 75 (2006) 082001.
[36] A. Ishizaki and G.R. Fleming, PNAS 106 (2009) 17255.
[37] D. E. Makarov and N. Makri, Chem. Phys. Lett. 221 (1994) 482.
[38] N. Makri and D. E. Makarov, J. Chem. Phys. 102 (1995) 4600.
[39] N. Makri and D. E. Makarov, J. Chem. Phys. 102 (1995) 4611.
[40] P. Nalbach and M. Thorwart, J. Chem. Phys. 132 (2010) 194111.
[41] M. Thorwart, J. Eckel, J.H. Reina, P. Nalbach and S. Weiss, Chem. Phys. Lett. 478 (2009) 234.
[42] S. Weiss, J. Eckel, M. Thorwart and R. Egger, Phys. Rev. B 77 (2008) 195316.
[43] M. Thorwart, P. Reimann and P. Hänggi, Phys. Rev. E **62** (2000) 5808.
[44] M. Thorwart, E. Paladino, and M. Grifoni, Chem. Phys. **296** (2004) 333.
[45] R. Bulla, N.-H. Tong and M. Vojta, Phys. Rev. Lett. 91 (2003) 170601.
[46] R. Bulla, H.-J. Lee, N.-H. Tong and M. Vojta., Phys. Rev. B 71 (2005) 045122.
[47] J. Prior, A.W. Chin, S.F. Huelga and M.B. Plenio, Phys. Rev. Lett. 105 (2010) 050404.
[48] A.W. Chin, A. Rivas, S.F. Huelga and M.B. Plenio, J. Math. Phys. 51 (2010) 092109.
[49] S. Hayward and N. G, Annu. Rev. Phys. Chem, 46 (1995) 223.
[50] A.J. Daley, C. Kollath, U. Schollwck and G. Vidal, J. Stat. Mech.: Theor. Exp. P04005 (2004).
[51] R. Rosenbach, J. Prior, A.W. Chin, S.F. Huelga and M.B. Plenio, In preparation
[52] K.H. Hughes, C.D. Christ and I. Burghardt, J. Chem. Phys. 131 (2009) 024109.
[53] K.H. Hughes, C.D. Christ and I. Burghardt, J. Chem. Phys. 131 (2009) 124108.
[54] M. Sarovar, A. Ishizaki, G.R. Fleming, K.B. Whaley, Nat. Phys. 6 (2010) 462.
[55] F. Fassioli and A. Olaya-Castro, New J. Phys. 12 (2010) 085006.
[56] A. Rivas, K.M.R. Audenaert, M.B. Plenio and S.F. Huelga, in preparation
[57] K.M.R. Audenaert and S. Scheel, New J. Phys. **10** (2008) 023011.
[58] V. Vedral and M.B. Plenio, Phys. Rev. A 57 (1998) 1619.
[59] K.M.R. Audenaert and M.B. Plenio, New J. Phys. 8 (2006) 266.
[60] J. Eisert, F.G.S.L. Brandao, K.M.R. Audenaert, New J. Phys. 9 (2007) 46.
[61] O. Gühne, M. Reimpell and R.F. Werner, Phys. Rev. Lett. 98 (2007) 110502.
[62] M. Owari, M.B. Plenio, E. Polzik, A. Serafini and M.M. Wolf, New J. Phys. 10 (2008) 113014.
[63] K. Jensen, W. Wasilewski, H. Krauter, T. Fernholz, B. M. Nielsen, A. Serafini et al, Nat. Phys. 7 (2011) 13.