Noise assisted excitation energy transfer in a linear model of a selectivity filter backbone strand

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Abstract
In this paper, we investigate the effect of noise and disorder on the efficiency of excitation energy transfer (EET) in a $N = 5$ sites linear chain with ‘static’ dipole–dipole couplings. In fact, here, the disordered chain is a toy model for one strand of the selectivity filter backbone in ion channels. It has recently been discussed that the presence of quantum coherence in the selectivity filter is possible and can play a role in mediating ion-conduction and ion-selectivity in the selectivity filter. The question is ‘how a quantum coherence can be effective in such structures while the environment of the channel is dephasing (i.e. noisy)?’ Basically, we expect that the presence of the noise should have a destructive effect in the quantum transport. In fact, we show that such expectation is valid for ordered chains. However, our results indicate that introducing the dephasing in the disordered chains leads to the weakening of the localization effects, arising from the multiple back-scatterings due to the randomness, and then increases the efficiency of quantum energy transfer. Thus, the presence of noise is crucial for the enhancement of EET efficiency in disordered chains. We also show that the contribution of both classical and quantum mechanical effects are required to improve the speed of energy transfer along the chain. Our analysis may help for better understanding of fast and efficient functioning of the selectivity filters in ion channels.

Keywords: selectivity filter, energy excitation transfer, dephasing

(Some figures may appear in colour only in the online journal)

1. Introduction
Energy or charge transfer is one of the most important phenomena in physical and biological systems. Life-enabling transport phenomena in the molecular mechanism of biological systems occur at scales ranging from atoms to large macro-molecular structures. Charge transfer through DNA [1] or charge and energy transfer processes in photosynthetic structures [2–5] are good examples in this context. Recently, the idea has been put forward that quantum mechanics might have a positive effect on the efficiency of energy or charge transfer in living systems. One of the most important effects of quantum mechanics in biological systems has been evidenced in the Fenna–Matthews–Olson (FMO) complexes [6] which are observed by experimental methods via ultrafast spectroscopy [3].

It has been shown that by using the unique properties of quantum dynamics up to the first order of perturbation theory, even small quantum mechanical contributions can enhance electron transport rates in metalloproteins by almost ten times, compared to analogous semiclassical models under certain conditions [7]. The classical theories of EET, built on stochastic diffusion to model the hopping motion of a photo-excited exciton, accounts inadequately for the speed and efficiency of the energy transfer measured in a series of recent landmark experiments [8]. In fact, taking a quantum mechanical perspective, can help capturing of the salient features of the efficient part of that transfer [8]. Moreover, it is found that under typical biological conditions the importance of quantum coherent transport is reduced due to the suppression of the coherent tunneling amplitudes and the presence...
of dephasing and incoherent tunneling, leading to diffusive-like electron transport [7]. The role of coherence and noise are more important than other phenomena such as entanglement, since it is concluded that even if entanglement exists in these structures, its role for the EET efficiency seems to be irrelevant, whereas the role of coherence might be important [9].

Natural systems, inevitably, suffer from various types of noise with internal and external sources, which perturb the intrinsic dynamics of the real systems. Noise exists everywhere, especially in the hot, wet and complex structures of biological systems. As a general expectation, noise is a destructive factor for any system, but in some living systems it is vice versa [10]. Here, we would like to study excitation energy transfer in a toy model of a strand of a protein (i.e. a linear harmonic chain) in the presence of noise via a quantum mechanical approach. It is known that in many ion-channel proteins, flow of ions through the pore is governed by a gate, comprised by a so-called selectivity filter that can be activated by electrical, chemical, light, thermal and/or mechanical interactions. The selectivity filter is believed to be responsible for the selection and fast conduction of particular ions across the membrane of an excitable cell. A selectivity filter is composed of four P-loop chains (P-loop or phosphate-binding loop is a motif in proteins that is associated with phosphate binding), and each strand is composed of the sequences of TGVYG amino acids (T(Threonine, Thr75), V(Valine, Val76), G(Glycine, Gly77), Y(Tyrosine, Tyr78), G(Glycine, Gly79)) linked by peptide units H–N=C=O (see figure 1). As a result, an extra site so-called ‘sink’ will be introduced at the end of the loop [10]. So, we consider a linear chain of \( N = 5 \) sites, composed of two level molecules. Each molecule can be stimulated to its excited state and the excitation energy for a single molecule. The dipole–dipole couplings between the molecules.

2. Structure and transport model

Since there are five main peptide units in the P-loop structure, we take \( N = 5 \). However, we are interested in measuring the amount of energy transported to the end of the P-loop strand. As a result, an extra site so-called ‘sink’ will be introduced at the end of the loop [10]. So, we consider a linear chain of \( N = 5 \) sites, composed of two level molecules. Each molecule can be stimulated to its excited state and the excitation energy for a single molecule. The dipole–dipole couplings between the molecules.

The paper is organised as follows. In section 2 the model is described and quantum transport equations in terms of Lindblad operators are introduced. Excitation energy transport calculations, in the absence and presence of noise, are given in section 3. In section 4, we present an alternative approach to find the contribution of classical dynamics in the efficiency of energy transfer. The results are summarised in section 5.

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Figure 1. P-loop strand of a selectivity filter: the amino acid molecular chains play the main role in conducting the ions. In the structure of the selectivity filter N–C=O is an amide group and C=O is a carbonyl group. Here we have considered each peptide unit H–N–C=O as one molecule. The P-loop strand is in the form of a chain of peptide units.

Figure 2. Schematic representation of excitation energy transfer through (top) an ordered chain in which the distances between sites are equal and (bottom) a disordered chain with random distances between the molecules.
\[ J_n = \frac{\tilde{J}_0}{d_{0,n+1}^3} \]  

in which \( \tilde{J}_0 \) contains the dipole moment and is set to unity (\( J_0 = 1 \)), \( d_{0,n+1} \) is the equilibrium distance between two neighbours. Since we consider the excitation in an open quantum system, therefore, energy dissipation due to interaction with the environment is inevitable. Markov approximation formulation of the energy loss due to dissipation, can be done by using the following Lindblad super-operator [10]:

\[ L_{\text{diss}} \rho = \sum_{n=0}^{N} \gamma_n [2\sigma_n^- \rho \sigma_n^+ - \{\sigma_n^+, \sigma_n^-, \rho\}], \]

where \( \rho \) is the total density matrix of the system, \( \sigma^+ (\sigma^-) \) is the creation (annihilation) operator of the excitation at site \( n \), \( \gamma_n \) is the dissipation rate at each site, and \( \{A, B\} = AB + BA \). In order to measure how much of the excitation energy is transferred along the chain (and not lost due to dissipation), we introduce an additional site, the sink, representing the final \((N + 1)\)th trapping site that resembles a reaction center, in a photosynthesis system [10]. The sink is populated via irreversible decay of excitation from the last site, \( N \). This approach is formally implemented by adding the following Lindblad operator to the master equation [10]:

\[ L_{\text{sink}} \rho = \gamma_{\text{sink}} [2\sigma_{N+1}^- \sigma_N^- \rho \sigma_{N+1}^+ - \{\sigma_{N+1}^+, \sigma_{N+1}^-, \rho\}]. \]

In which \( \gamma_{\text{sink}} \) denotes the absorption rate of the sink, for which we select the typical values \( \gamma_{\text{sink}} = 0.1 \) in this work. Later, we will discuss the dependence of the results on \( \gamma_{\text{sink}} \).

In order to calculate the efficiency of energy transfer given by the asymptotic population of the sink, it is necessary to integrate the following master equation (\( \hbar = 1 \)):

\[ \frac{\partial \rho}{\partial t} = i[\rho, H] + L_{\text{diss}} \rho + L_{\text{sink}} \rho. \]

Here, an excitation is injected at the first site, i.e., \( \rho(0) = |1\rangle \langle 1| \) and we are interested in finding how much of the excitation can be transferred to the sink, so we have to find \( P_{\text{sink}}(t) = \langle N+1 | \rho(t) | N+1 \rangle \), which is called \textit{Sink population} (at time \( t \)). In this paper, we use the Python package QUTIP [13] to numerically solve the Lindblad master equations. In our numerical simulations, all energies, time-scales, and rates will be expressed in units of \( \epsilon \), and thereby we consider \( \epsilon = 1 \).

### 3. EET in ordered and disordered chains

In this section we study the quantum excitation energy transfer in the static chains in which the distances between sites are time independent. The ordered static chain is a chain in which the distances between sites are equal and the couplings between sites are frequency-independent and do not vary with time. A disordered static chain is the same as ordered static chain but the distances between sites are chosen randomly (see figure 2).

The coupling between neighbouring sites is expressed as the following:

\[ J_n = \frac{\tilde{J}_0}{d_{0,n+1}^3}, \]

\[ \gamma_{\text{diss}} = \frac{\tilde{J}_0}{[d_{0,n+1}^2]}. \]

Where \( \tilde{J}_0 \) is the dipole moment and \( d_{0,n+1} \) is the equilibrium dimensionless distance between the sites \( n \) and \( n+1 \), which is taken to be unity for ordered chain. For the disordered chain, we use the relative ratios of distances based on the real data obtained from the distances between amino acids in one strand of the backbone of the selectivity filter of KcsA ion channels. In the mentioned structure, the distances between neighbouring sites are, \( r_{0,1,2} = 2.6 \AA, r_{0,2,3} = 3.1 \AA, r_{0,3,4} = 2.6 \AA \) and \( r_{0,4,5} = 4.3 \AA \) [12], therefore, dividing the distances over the minimum one 2.6 \AA\, gives us the relative distances \( d_{0,1,2} = 1, d_{0,2,3} = 1.19, d_{0,3,4} = 1 \) and \( d_{0,4,5} = 1.65 \). Energy population in the sink is calculated using the method explained in the section 2. As a matter of fact, each molecule feels a different environment, hence the local dissipation rates \( \gamma_n \) depend on the sites, nevertheless for the sake of simplicity and due to so far unavailable experimental data, we will later assume them to be uniform \( \gamma_n = \gamma_{\text{diss}} \). In order to pick a typical value for dissipation rate, we fixed \( \gamma_{\text{sink}} = 0.1 \) in equation (5) and calculated the sink population in terms of \( \gamma_{\text{diss}} \). The results represented in figure 3, show the rapid decaying of sink population with dissipation rate coefficient in both disordered and ordered static chains. Since we are interested in a system with efficient energy transfer, hence in the rest of the paper we select a small value \( \gamma_{\text{diss}} = 0.001 \) for the dissipation rate.

With such a selection for dissipation, the sink population is plotted versus time in figure 4, for ordered and disordered chains. It can be seen that population for disordered chain is clearly less than the ordered one, which can be explained in terms of the quasi-localization of states in a random chain. Indeed, all the eigenstates of the Hamiltonian (1) are localized for an infinite randomness, as a result of the Anderson localization theory [14]. In fact, the randomness in the disordered

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Figure 4. Temporal variation of sink population for static ordered (blue (black) solid line) and disordered chain (red (grey) solid line). The states are extended. The states with localization length comparable with system size can be considered as quasi-localized. The existence of such states can be easily verified by expanding a given wave function in terms of the eigenstates of the model Hamiltonian. Decomposing the initial excitation wave pocket, $|1\rangle$, into the eigenstates of the original Hamiltonian $H$, we find for the ordered chain

$$
|1\rangle = -0.5(-0.5, 0.5, 0.0, -0.5, 0.5) + 0.57(0.58, 0.0, -0.58, 0.0, 0.58)
+ 0.5(-0.5, -0.5, 0.5, 0.0, 0.5, 0.5) + 0.3(0.29, 0.5, 0.58, 0.5, 0.29)
+ 0.3(0.29, -0.5, 0.58, -0.5, 0.29),
$$

and for the disordered chain

$$
|1\rangle = 0.13(0.13, 0.0, -0.22, 0.0, 0.97) + 0.41(0.41, 0.56, 0.57, 0.43, 0.07)
- 0.56(-0.57, 0.43, 0.39, -0.56, 0.16)
- 0.56(-0.57, -0.43, 0.39, 0.56, 0.16) + 0.41(-0.41, -0.56, 0.57, -0.43, 0.07).
$$

Equation (7) clearly shows that the amplitude of the initial wave pocket at the end-site is significantly high in all the eigenstates of the Hamiltonian for the ordered chain. However, in the case of the disordered chain, equation (8) indicates that the amplitude of the initial excitation pocket is very small in the final site, for some eigenstates and so these modes are approximately localized within the first four sites. Such quasi-localized modes spend much time inside the chain and then leak out to the environment because of dissipation, hence losing their ability to highly corporate in the energy transfer into the sink.

To explicitly show the localization effect on the energy transfer, we plot the time dependence energy density in the first two sites in the left-(a) and right-(a) panels of figure 5 for ordered and disordered chains, respectively. The temporal behaviour of energy populations in the other sites is similar to that in the first two sites and is not shown for the sake of clarity. It can be clearly seen that the energy population in sites 1 and 2 persists much longer in the disordered chain than in the ordered chain.

Now we proceed to investigate the effect of noise on the quantum energy transfer along the chain. Real systems are open and interact with the environment, so it is reasonable to assume that the environment is dephasing which means it is noisy and has a destructive effect on quantum coherence in the system. The dephasing term can be incorporated to the master equation, using the following Lindblad form [10]

$$
L_{\text{deph}} \rho = \sum_{n=1}^{N} \gamma_{\text{deph}}[2a_{n}^{+}a_{n}\rho - a_{n}^{+}a_{n}\rho - \{a_{n}^{+}a_{n}, \rho\}]
$$

where $\gamma_{\text{deph}}$ is the dephasing rate coefficient. In general, one expects decreasing population after adding dephasing term.

Figure 6 illustrates variation of the sink population, as $t \to \infty$, versus dephasing rate for the ordered and disordered chains. As we expected, dephasing (i.e. noise) decreases population (i.e. efficiency) of the ordered chain. However, something different is observed for the static disordered chain; it is seen that the sink population does not behave monotonically versus dephasing rate, in such a way that noise is able to increase the efficiency of energy transfer and reach it to a maximum efficiency for $\gamma_{\text{deph}} \sim 0.2$. The reason for noise-assisted energy transfer in the disordered chain is the weakening of the localization, as a result of dephasing which reduces the constructive coherent back-scatterings responsible for such a localization, hence leading to the enhancement of the efficiency of energy transfer. Panels (b) in figure 5 evidently represent the demolishing effect of dephasing on the constructive back scattering in both ordered and disordered chains. As can be seen from the left-(b) panel of figure 5, the destruction of Anderson localization in the disordered chain leads to remarkable enhancement in the amount of the sink population, and also the speed of energy transfer.

In order to gain insight into the effect of possible values of the absorption rates of the sink, $\gamma_{\text{sink}}$, and dephasing rates, $\gamma_{\text{deph}}$, on the energy transfer efficiency, we illustrate the density plots of sink population for the ordered (figure 7, left) and disordered (figure 7, right) chains. This figure shows there is no region in the parameter space, $\gamma_{\text{sink}} = \gamma_{\text{deph}}$, for the noise-assisted energy transfer in the ordered chain, while we see
that such a phenomenon occurs in the disordered chain in the region with $\gamma_{\text{sink}} \leq 0.5$.

4. Hybrid quantum-classical dynamics

We have demonstrated that the collaborative interplay between the quantum-coherent excitation and the mechanical motion of the molecules would enhance the excitation energy transfer through the linear chain. It is already concluded that a closer look at the involved dimensions and energetics of the process reveals that the underlying mechanism for ion transmission and selectivity might not be entirely classical [15]. Recently, it was demonstrated theoretically that, based on the time and energetic scales involved in the selectivity filter, the ion selectivity and transport cannot be entirely a classical process but involves quantum coherence [16]. In this section we pursue an alternative approach to evaluate the contribution of the classical and quantum mechanical effects in the efficiency of energy transfer across the chain. For this purpose, we use Kossakowski–Lindblad master equation [19, 20] in the following form:

$$\frac{d \rho}{dt} = -(1 - \eta) i[H, \rho] + \eta \sum_{ij} [L_{ij} L_{ij} \rho L_{ij} \rho - 1/2 \{L_{ij} L_{ij}, \rho\}],$$

(10)

where $\eta$ is a measure for the classical contribution of the energy transfer. If $\eta = 0$ we have a pure quantum energy transfer and if $\eta = 1$ the energy transfer is fully classical [19], and for the other values of $\eta$ (between 0 and 1) we have a joint cooperation between classical and quantum mechanical effects. In the above equation, $L_{ij} = T_{ij} |i\rangle \langle j|$, where $|i\rangle$ denotes the real space basis state and we select $T_{ij} = J_0/d_{ij}$, in which $J_0 = 1$ and $d_{ij}$ is selected as the real normalized distance between the sites $i$ and $j$ (amino acids in the p-loop strand) in the disordered chain and $d_0 = 1$ for the ordered chain.

Here we neglect the dissipation and again add $L_{\text{sink}}$ to the above equation (10) and calculate the saturation time $t_s$ (the time in which all of the first injected energy is transferred to the sink) versus parameter $\eta$. As shown in figure 8, $t_s$ is not very sensitive to $\eta$ in the ordered chain, however in the disordered chain we observe that $t_s$ rapidly drops by increasing the classical part of the energy transfer dynamics. The optimal stationary time is obtained for $\eta \sim 0.5$, meaning that the maximum efficiency in the speed of energy transfer is acquired by approximately equal contribution of classical and quantum mechanical effects.

5. Discussion and conclusion

Ion channels are proteins in the membranes of excitable cells that cooperate for the onset and propagation of electrical signals across membranes by providing a highly selective conduction of charges bound to ions through a channel like
structure. The selectivity filter is a part of the protein forming a narrow tunnel inside the ion channel which is responsible for the selection process and fast conduction of ions across the membrane [18]. Certainly, the magnitude of the thermal fluctuations of the backbone atoms forming the selectivity filter is large relative to the small size difference between Na and K, raising fundamental questions about the mechanism that gives rise to ion selectivity. This suggests that the traditional explanation of ionic selectivity should be re-examined [17]. Recently, Vaziri et al [15] and Ganim et al [16] proposed the presence of quantum coherence in $K^+$ ion-channels, in their backbone amide groups that can play a role in mediating ion-conduction and ion-selectivity in the selectivity filter. In summary, we analysed quantum excitation energy transfer (EET) in a linear chain composed of five sites, as a toy model for one strand of selectivity filter backbone. The inter-site separations are adjusted to be proportional to the distances between peptide units in the selectivity filter. EET is studied both in the absence and presence of dephasing noise. Comparison of the result with those obtained in an ordered chain, indicates that disorder in such systems always has a destructive role in EET, because of their role in multiple coherent back-scatterings which leads to the quasi-localization of some excitation modes within the chain. When dephasing is introduced, it is found that noise has a destructive effect in EET in ordered chains. Nevertheless, for disordered chains it is shown that the noise is able to significantly increase the efficiency of energy transfer across the chain either in amount or speed. The main message of this work is the significance of dephasing in the efficiency of quantum energy transfer in disordered chains. Living systems are mostly disordered and in some cases are very efficient, so it is possible in such systems that noise has a key role for efficient energy transfer through their structures, e.g. selectivity filter backbone.

However, there is an open question and a challenge concerning our work as well as all previous works regarding the quantum EET in biological systems, which is how the exciton is trapped in the sink. This is a separate but related problem, since without trapping, the excitation will persistently oscillate between sites under the action of the unitary evolution. In general, we have simplifications for the selectivity filter backbone and thus we should consider more realistic parameters (i.e in the presence of ions [21]) to make sure about the constructive role of noise and disorder, which will be the next research prospect for the continuation of our work.

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