Two-level system with a thermally fluctuating transfer matrix element: Application to the problem of DNA charge transfer

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Charge transfer along the base-pair stack in DNA is modeled in terms of thermally-assisted tunneling between adjacent base pairs. Central to our approach is the notion that tunneling between fluctuating pairs is rate limited by the requirement of their optimal alignment. We focus on this aspect of the process by modeling two adjacent base pairs in terms of a classical damped oscillator subject to thermal fluctuations as described by a Fokker-Planck equation. We find that the process is characterized by two time scales, a result that is in accord with experimental findings.

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I. INTRODUCTION

In spite of the fact that a decade has passed since the first definitive observation of charge transfer along the DNA base-pair stack [1], the detailed properties of this process have not been definitively elucidated. This is partly due to the inherent complexity of the molecular structure of DNA, and to the large number of external and intrinsic factors that exert an influence on DNA structure and behavior. The current unsettled situation also reflects the absence of an overall agreement on the precise mechanism by which this charge transport takes place. One of the key issues that awaits full illumination is the role of disorder—both static and dynamic—on the propagation of charge along the base-pair stack. A related, and quite fundamental, question is whether charge transport is a coherent quantum mechanical process, like conduction of electronic charge against a static, charge transport is a coherent quantum mechanical process. One of the key issues that awaits full illumination is the role of disorder—both static and dynamic—ion the propagation of charge along the base-pair stack. A related, and quite fundamental, question is whether charge transport is a coherent quantum mechanical process, like conduction of electronic charge against a static, or deformable, background, or whether it it takes place as fundamentally incoherent transport, as a variation of the random walk. The answers to these and other questions will have a significant impact on both our understanding of the biological impact of charge transport in DNA and the development of applications based on this phenomenon.

Despite the often contradictory results of experimental investigations [2, 3, 4, 5, 6, 7], a few conclusions seem inescapable. The first is that long-range charge transport along the base-pair stack depends quite strongly on the sequence of the base pairs [5]. In addition, base-pair mismatches can have a significant deleterious effect on charge transport [2, 3] (see, however [4, 5]). Furthermore, strands of DNA display considerable disorder, both static [1] and dynamic [2, 3, 4, 5, 6]. Finally, several sets of experiments on ensembles of short DNA strands have uncovered an unusual two-step charge transfer process [4, 5]. These studies focus on fluorescent charge donors intercalated in DNA oligostrands. As the charge migrates towards the acceptor, the fluorescence is quenched and the rate of migration is determined by the decaying fluorescence profile. The data reveals that this decay process occurs according to two characteristic time-scales which are separated by more than an order of magnitude [4, 7]. Any model that purports to explain charge transport must take all this into account.

In this paper, we discuss a model for short range charge transport along a base pair stack that undergoes substantial structural fluctuations. The process occurs via thermally-assisted quantum mechanical tunneling of charge carriers from one base pair to the next, under the assumption that this tunneling is properly characterized as occurring in the presence of a dissipative environment. A key conjecture is that charge transfer takes place only when the neighboring pairs are in a state of optimal “alignment”, and that this alignment is statistically unlikely in thermodynamic equilibrium. As we will see, this conjecture leads in a natural way to a model exhibiting the dual-time-scale feature described above. Additionally, the model generates predictions that can be readily tested. We shall relate the problem at hand to the dynamics of a simple two level system (TLS), realized by a donor and an acceptor state.

In Section I, we briefly recapitulate what is known about the tunneling process in the presence of friction for a TLS system. We also quantify our notion of a coordinate θ associated with the “alignment” of adjacent base pairs and of the influence of the dynamics of this new coordinate on charge transfer. Section II specifies the model for describing a generic collection of two-level systems (TLS), initially in the donor state and characterized by a fluctuating alignment variable θ. The probability distribution of donor states, W(θ, θ, t) obeys a Kramers equation with a sink term due to charge transfer to the acceptor. The rate of charge transfer will be expressed by the fluctuating rate Γ(θ). This Kramers expression is recast into the form of a Volterra equation with the use of a Lie-Algebra approach defined on the Hilbert space of the eigenstates of the Kramers equation for Γ(θ) = 0. We will discuss limiting cases of the solution to obtain physical insight and to reveal the two-time-scale decay of the probability distribution due to the sink term. We conclude in Section III with a discussion of the possible application of our results to charge transfer in strands of DNA consisting of several base pairs.

The key result of our calculations lies in the determi-
nation of \( P(\theta^*, t) \), the probability distribution of donor states evaluated at the optimal configuration \( \theta^* \) and with the \( \theta \) variable integrated out. Indeed, under the assumption that the tunneling process is most effective at \( \theta \sim \theta^* \), this quantity is directly related to the fluorescence intensity \( I(t) \) of the base pair complexes, as probed by J. Barton and A. Zewail [16, 17], through the following:

\[
I(t) = I_0 \left[ 1 - \Gamma \right] \int_0^t P(\theta^*, t') dt'. \tag{1}
\]

The quantity \( I_0 \) of the above relationship is a proportionality constant and \( I \) is the integrated rate of transfer to the acceptor. We shall determine the double exponential character of \( P(\theta^*, t) \), and hence of \( I(t) \), in qualitative agreement with the experimental findings. The conjectures made on the existence of an optimal and unlikely configuration \( \theta^* \) will be crucial in obtaining the two stage decay process, a result that justifies the assumptions made.

The model we shall construct is obviously not restricted in application to DNA oligostrands. Using our results, we may conclude that in an ensemble of generic systems the migration of a particle from donor to acceptor proceeds statistically as a two-time scale process, provided the transfering process is of rare occurrence.

## II. THE TUNNELING PROCESS

The process of charge transfer from a donor site to an acceptor site—a two-level system—is ubiquitous in biochemical and physical phenomena [18]. It occurs under a broad variety of spatio-temporal conditions. Chemical bond formation or destruction, ATP production in photosynthetic reactions, or the operation of semiconducting devices, all involve the transfering of charges to and from specific sites, via thermal activation or quantum-mechanical tunneling through an energy barrier. Because of its intrinsic nature, charge transfer via quantum-mechanical tunneling takes place on a length scale of up to tens of angstroms [19]; larger distances are possible if other transport mechanisms are involved. These include thermal hopping among sites, which are typical in disordered systems, the creation of conduction bands in metals, or of lattice distortions of polaronic type in specific systems.

Quantum-mechanical tunneling from a donor site to an acceptor site is quite simply represented by a two-level system (TLS) [20]. In this description, the tunneling particle is limited to being in the donor or in the acceptor state, while the other degrees of freedom of the system, nuclear for instance, describe the charge potential energy.

The energetic profile of the system is thus characterized by a multidimensional surface of which the acceptor and the donor states constitute relative minima, separated by a barrier. Of the many existing degrees of freedom, it is often possible to identify a “reaction coordinate” \( y \) such that the energy barrier between donor and acceptor is minimized along this specific direction. The progress of the reaction is then dominated by the evolution along this coordinate and the potential energy surface can be reduced to an effective one-dimensional curve.

In certain systems the physical interpretation of the reaction coordinate is immediate: it may be the relative bond length in two diatomic molecules, or solvent polarization around the donors and acceptors [22]. It is not an easy task to give a physical interpretation of the reaction coordinate in the case of DNA base pairs because of the many possibilities involved— intra-base distance, mobile counter-ion concentration, solvent concentration, or a combination of all the above. A possibility is offered by Ref. [22] where it is suggested that the most relevant quantity is the interaction of the charge with the polar water molecules of the solvent. In this paper we shall refer to the reaction coordinate \( y \) in most general terms.

A common representation of tunneling with dissipation is through the spin-boson formalism [20]. The donor and acceptor states are represented by means of a pseudo spin, which points up when the charge is in the donor state and down otherwise. The Hamiltonian of the system is given by:

\[
H_{ET} = \tau \sigma_x + \frac{P^2}{2M} + V(y, \sigma_z) + H_{bath}, \tag{2}
\]

where

\[
V(y, \sigma_z) = \frac{1}{2} M \omega^2 (y + y_0 \sigma_z)^2 + \frac{1}{2} \epsilon \sigma_z, \tag{3}
\]

FIG. 1: This figure illustrates the nature of the tunneling transition. The two parabolic curves shown correspond to the two versions of the potential \( V(y, \sigma_z) \) in Eq. (4), one corresponding to the “donor” state in which the tunneling particle is on one site and the other to the “acceptor” state, in which the particle is on the other one. The two energies \( E_f \) and \( E_h = E_f - \epsilon \) referred to in the text are the forward and backwards barrier energies respectively. The horizontal axis corresponds to the reaction coordinate, \( y \).
and $\sigma_z$ are the Pauli matrices. The charge in the donor (up) state corresponds to the potential $V(y, +)$ whose equilibrium reaction coordinate is $-y_0$, and the converse state corresponds to $V(y, -)$, whose stable minimum is at $y_0$. The $H_{\text{bath}}$ term represents contributions to the Hamiltonian of a dissipative environment coupled to the reaction coordinate. Figure 1 illustrates the meaning of the potential $V(y, \sigma_z)$ in the effective Hamiltonian of Eq. (3). The curve marked A corresponds to the potential term in the donor state, while the curve marked B represents the potential function in the acceptor state.

This model has been thoroughly analyzed in the work by Garg et al. [23] based on earlier work by Leggett [24]. A similar analysis, but within a more chemical framework, is presented by Marcus et al. [25]. Energy conservation requirements that charge transfer takes place only when the reaction coordinate is close to the degeneracy point $y = y^*$ for which $V(y^*, +) = V(y^*, -)$; once the degeneracy point is reached, charge transfer is possible only because of the non zero off-diagonal tunneling matrix elements $\tau$.

The tunneling rate $\Gamma$ from donor to acceptor, is calculated in the above references. For moderate dissipation of the reaction coordinate, it is given by:

\[
\Gamma = \frac{\tau^2}{h} \left( \frac{\pi}{E_r k_B T_{\text{eff}}} \right)^{\frac{1}{2}} \left( e^{-E_f/k_B T_{\text{eff}}} + e^{-E_b/k_B T_{\text{eff}}} \right)
\]

where the reorganization energy $E_r$ and the energy barriers $E_f$ and $E_b$ depend on the details of the potential described by the reaction coordinate. In the limit of high temperatures $T_{\text{eff}}$ reduces to the usual temperature $T$, whereas in the opposite limit the quantity is temperature independent.

The novelty explored in this paper is the introduction and investigation of the effect of a second reaction coordinate, $\theta$, governing the charge transfer process and coupled not to the energy, but to the off-diagonal tunneling element $\tau$, hitherto been treated as a constant, and which we now write $\tau(\theta)$.

This new coordinate reflects the conjecture that in the case of DNA the tunneling matrix element is highly sensitive to the donor-acceptor relative configuration. Charge transport along DNA in fact occurs along the stacked base pairs by means of overlapping $\pi$ orbitals, and at room temperature, these base pairs strongly fluctuate with respect to each other through variations of the twist, tilt and roll parameters [26]. The existence of base pair fluctuations for DNA in solution is very well established, and is corroborated by experimental [12] and molecular dynamics studies [13, 14, 15]. For such a highly asymmetric system such as DNA, fluctuations in the relative orientation of donors and acceptors affect the magnitude of the orbital overlap between pairs, and the new collective coordinate $\theta$ embodies the effects of these fluctuations.

We will also assume that the $\theta$ variable is slowly varying compared to the motion of the reaction coordinate $y$, so as to define the lowest energy scale of the system. We may then separate the motion of the two reaction coordinates in a Born-Oppenheimer spirit. Charge transfer will be assumed to be instantaneous once the optimal $\theta = \theta^*$ value is reached, and a purely classical framework will be utilized for the $\theta$-dynamics. The new reaction coordinate $\theta$ need not necessarily be pictured as a geometrical one, although this is the framework we will be utilizing in this paper. Just as in the case of the $y$ reaction coordinate, $\theta$ may be associated to the particular chemical environment of the molecule or to any other quantity influencing the strength of the tunneling element $\tau$ between the donor and the acceptor sites.

The Hamiltonian describing the system thus, is a modified version of the spin-boson Hamiltonian introduced in Eq. (4) with a $\tau(\theta)\sigma_z$ off-diagonal term, as also described in earlier work [23]. In order for charge transfer to take place, we will assume that the reaction coordinate coupled to the energy must be close to the degeneracy point $y = y^*$, and, also, that the $\theta$ coordinate must be in the neighborhood of an optimal value $\theta^*$, which maximizes the tunneling amplitude. The physical picture to associate to this requirement is that the relative “alignment”, $\theta$, does not favor charge transfer unless an optimal configuration is reached: $\tau(\theta) \approx 0$ unless $\theta \approx \theta^*$. This conjecture will prove to be crucial in yielding the two time-scale charge transfer of references [16, 17].

In analogy to the experimental work cited above, we consider a collection of such two-level systems, with the charge initially located on the donor site. Each one of these systems is associated to a particular $\tau(\theta)$ and through Eq. (4) to a particular $\Gamma(\theta)$ rate. Our objective is to determine the mechanisms of charge transfer taking into account the $\theta$ time evolution and the $\Gamma(\theta)$ rates according correspondingly distributed. We shall assume the $\theta$ dynamics to be governed by small, Langevin type random fluctuations. At $t = 0$, when the external charge is injected on the donor site, the distribution of $\theta$ values is the usual Boltzmann distribution. If the occurrence of the optimal $\theta^*$ configuration is relatively unlikely, we will indeed be able to show that the transfer process is characterized by a two time scale migration of the initial donor population.

The emergence of two time scales in the transfer process can be physically explained as follows. The existence of an initial non-zero population of TLS presenting the optimal value $\theta^*$, ensures that rapid tunneling to the acceptor. The $\theta$ distribution is thus depleted of population at the special value and other transitions are forbidden to take place. The other TLS will tunnel to the acceptor only after the system has re-equilibrated and re-populated the optimal configuration, a process which is slow, because of the assumption that the optimal configuration is a relatively unlikely one. Hence, the existence of a fast, initial decay followed by a slower decay process.
III. THE TLS AND $\theta$ FLUCTUATIONS

A. The model

Consider a collection of TLS which at the initial time $t = 0$ are all in the up-donor configuration, and characterized by the angular parameter $\theta$. Let us denote by $W(\theta, \dot{\theta}, t)$ the TLS population remaining in the up-donor state at time $t$ and for which the collective angular variable and its velocity are specified.

The physical requirement that $\theta$ be randomly, classically, fluctuating in time, translates into the fact that $W(\theta, \dot{\theta}, t)$ must evolve according to a Fokker-Planck type equation as dictated by standard Langevin theory. To this probability evolution equation we must add an additional depleting term, that which represents tunneling to the donor site as given by the $\Gamma(\theta)$ term discussed above.

Different scenarios are possible for the $\theta$ dependence of $\tau$ and hence of $\Gamma$. As discussed in the above section we shall focus on the particular situation in which tunneling is possible only for a very specific subset of energetically unfavorable $\theta$ values. In this picture, tunneling is allowed only if donors and acceptors reach an optimal—but unlikely—orientation one with respect to the other. By including the tunneling term in the time evolution equation for $W(\theta, \dot{\theta}, t)$ we obtain a modified Fokker-Planck equation that may be used to approach any physical system in which the presence of a depleting term competes with the usual Langevin fluctuations. The most natural choice for the $\theta$ motion, the one we shall discuss in the remainder of this paper, is that of a damped harmonic oscillator. We shall see that starting from an initially equilibrated system in which the $\theta$ distribution is the Boltzmann one, the insertion of the tunneling term will result in the emergence of the two time scales discussed above.

The goal of the next subsections will be to determine $W(\theta^*, u, t)$, and in particular its integration with respect to the $u$ variable. As described in the introduction in fact, it is this quantity that is directly related to the experiments we wish to model by means of Eq. (1).

B. Kramers equation with a sink term

The generic damped harmonic oscillator subject to random noise responds to the following Langevin-type equations:

$$\dot{\theta} = u; \quad \dot{u} = -\gamma u - \Omega^2 \theta + \eta(t),$$

(5)

where the stochastic force $\eta(t)$ is assumed to be a zero-mean gaussian and whose correlation function is dictated by the fluctuation-dissipation theorem for classical variables:

$$\langle \eta(t) \eta(t') \rangle = \frac{2\gamma k_B T}{I} \delta(t - t') = 2q \delta(t - t').$$

(6)

The corresponding Fokker-Planck equation may be written by identifying [23] the proper coefficients in the Kramers-Moyal expansion from Eq. (3) and is generally referred to as the Kramers equation. This equation governs the time evolution of the distribution, $W(\theta, u, t)$, of an ensemble of systems obeying the equations of motion (4). It takes the form:

$$\frac{\partial W}{\partial t} = -u \frac{\partial W}{\partial \theta} + \frac{\partial}{\partial u} \left[(\gamma u + \Omega^2 \theta)W\right] + \frac{\partial^2 W}{\partial u^2}.$$ 

(7)

The above equation is thoroughly analyzed in [30], where assuming an initial probability distribution $W(\theta, u, 0) = \delta(\theta - \theta^*) \delta(u - u')$, the probability $W(\theta, u, t)$, as well as other relevant statistical quantities, are obtained. At equilibrium Kramers equation is solved by the time independent Boltzmann distribution, $W(\theta, u, t) = \psi_{0,0}(\theta, u)$ with:

$$\psi_{0,0}(\theta, u) = \frac{\gamma \Omega}{2 \pi q} \exp \left[-\frac{\gamma}{2q} \left(u^2 + \Omega^2 \theta^2\right)\right].$$

(8)

Under the assumptions discussed earlier, the probability distribution function $W(\theta, u, t)$ for a particle localized on the donor site and describing an effective angle $\theta$ with its neighbor, will be described by the time evolution equation for a collection of damped oscillators subject to a decay term $\Gamma$, representing tunneling to the acceptor. The latter term is appreciable only for a specific value of the $\theta$ coordinate $\theta^*$:

$$\frac{dW}{dt} = HW - \Gamma(\theta, u, t) W.$$ 

(9)

The $H$ term is the differential operator that stems from the right hand side of Eq. (4). We shall assume the decay term to be introduced at time $t = 0$, prior to which the system had attained its equilibration state. In other words, we choose the initial distribution $W(\theta, u, 0)$ to be Boltzmann-like, as expressed in Eq. (3). For simplicity, we choose $\Gamma(\theta)$ to be independent of $u$ and of $t$ and to be a gaussian centered on $\theta^*$ and with width $\sigma$:

$$\Gamma(\theta) = \frac{\kappa}{\sqrt{2 \pi \sigma}} \exp \left[-\frac{(\theta - \theta^*)^2}{2\sigma}\right].$$

(10)

The coefficient $\kappa$ contains the physical parameters of temperature and energy as expressed in Eq. (4). We also impose the constraint that at $t = 0$ the optimal value $\theta^*$ carries a small Boltzmann weight. This is equivalent to the physical assumption that the occurrence of particle tunneling is a rather unlikely event, and that the system tends to relax to $\theta$ values that are far from the tunneling point. We also impose the width of the decay gaussian $\sqrt{\sigma}$, to be small compared to $\theta^*$, so that $\Gamma(\theta)$ is highly peaked around the optimal configuration value $\theta^*$: $\sqrt{\sigma} \ll \sqrt{q/\gamma \Omega^2} \ll \theta^*$. 


In the following subsections we will solve Eq. (10) for the early and long time regimes. The general solution for arbitrary times is contained in the appendix. The coupling of the system to the orientational degree of freedom along the lines discussed above, manifests itself very clearly in the unusual time dependence of the probability distribution. Two different decay rates in fact arise, with a rapid initial decay of the donor population \( W(\theta, u, t) \) followed by a slower transfer process. The ratio of these two time scales, and the main result of this analysis is succinctly expressed by Eq. (27) in terms of all the physical parameters of this system.

C. Short time regime

In order to determine the asymptotic behavior of \( W(\theta, u, t) \) in the early time regime, we consider Eq. (10) with the gaussian choice of \( \Gamma(\theta) \) and we perform a multiple time scale analysis \([33]\). This is carried out by introducing a new ad-hoc variable \( \xi = \Gamma(\theta)t \), into the probability distribution, and by seeking solutions in the form \( W(\theta, u, t, \xi) = W_0(\theta, u, t) + \Gamma(\theta) W_1(\theta, u, t, \xi) + \ldots \). The Fokker-Planck equation is thus expanded in powers of \( \Gamma(\theta) \) and, for the zeroth and first order terms, it yields:

\[
\begin{align*}
\frac{\partial W_0}{\partial t} - HW_0 &= 0, \\
\frac{\partial W_1}{\partial t} - HW_1 &= -\left[\frac{\partial W_0}{\partial \xi} + W_0\right] + u\Gamma^{-1}\frac{\partial \Gamma}{\partial \theta} W_1.
\end{align*}
\] (12)

Note that the partial derivative with respect to \( t \) in the above equations treats \( \xi \) as an independent variable. The solution to the first equation is expanded in terms of the complete set of functions \( \Psi_{m,n}(\theta, u, t, \xi) \) that solve Eq. (11) - obtained in Eq. (A3) and Eq. (A9) of the appendix - with coefficients \( A_{m,n} \) that depend on \( \xi \), i.e:

\[
W_0(\theta, u, t) = \sum_{m,n} A_{m,n}(\xi) \Psi_{m,n}(\theta, u) e^{-\lambda_{m,n}t}.
\] (13)

Substituting this solution for \( W_0 \) into Eq. (12), the inhomogeneous term in square brackets becomes:

\[
-\sum_{m,n} \left[\frac{\partial A_{m,n}}{\partial \xi} + A_{m,n}\right] \Psi_{m,n}(\theta, u) e^{-\lambda_{m,n}t}.
\] (14)

If this were the only term present on the right hand side of Eq. (12), then \( W_1(\theta, u, t, \xi) \) would contain a secular term in its solution of the type:

\[
W_1(\theta, u, t) \sim -\sum_{m,n} \left[\frac{\partial A_{m,n}}{\partial \xi} + A_{m,n}\right] \Psi_{m,n}(\theta, u) e^{-\lambda_{m,n}t}.
\] (15)

Such a solution will eventually exceed the “leading order” one. We determine the coefficients \( A_{m,n} \) by requiring that there be no secular term in the solution to the equation. It is precisely this constraint that constitutes the underlying idea of multiple scale analysis. The above condition translates into requiring that the non-homogeneous term within parenthesis in Eq. (12) or equivalently in Eq. (13) vanish:

\[
\frac{\partial A_{m,n}(\xi)}{\partial \xi} = -A_{m,n}(\xi).
\] (16)

We now solve for \( A_{m,n} \). Imposing the initial condition \( W(\theta, u, 0) = \psi_{0,0}(\theta, u) \) and reinserting \( \xi = \Gamma(\theta)t \) the solution reads:

\[
W_0(\theta, u, t) = \psi_{0,0}(\theta, u) \exp \left[-\Gamma(\theta)t\right].
\] (17)

The above is a zero-th order approximation to the full problem presented in Eq. (12) to the extent that the effect of \( H \) acting on \( \Gamma(\theta) \) can be neglected with respect to \( \Gamma(\theta) \) itself. In other words, Eq. (17) is an approximate solution as long as:

\[
t \ll \frac{\Gamma(\theta)}{|u\Gamma(\theta)|} = \frac{\sigma}{|u(\theta - \theta^*)|}.
\] (18)

This equation is valid only under the conditions expressed in Eq. (18) and up to \( t \approx \Gamma^{-1}(\theta) \). For this time limitation to be meaningful, it is necessary that the width of the decay term \( \sqrt{\sigma} \) be finite. In the limit that the width vanishes the above analysis fails, since the expansion parameter diverges. At time \( t \sim 0 \) we cannot approximate \( \Gamma(\theta) \) by a strict delta function. Note that for \( \theta \sim \theta^* \), the tunneling point, and for finite \( u \) the condition arising from the multiple scale analysis \( t \approx \sqrt{2\pi\sigma}/\kappa \) is the most stringent one, and the probability distribution is approximated by:

\[
W(\theta^*, u, t) = \psi_{0,0}(\theta^*, u) \exp \left[-\frac{\kappa t}{\sqrt{2\pi\sigma}}\right].
\] (19)

We now perform an integration over the \( u \) variable on both sides of Eq. (17) and obtain an approximation for the distribution probability function \( P(\theta, t) = \int_{-\infty}^{\infty} W(\theta, u, t) \ du \):

\[
P(\theta, t) \approx \psi_{0}(\theta) \exp \left[-\Gamma(\theta) t\right].
\] (20)

where \( \psi_{0}(\theta) \) is the Boltzmann distribution associated to the \( \theta \) variable \( \psi_{0}(\theta) = \int_{-\infty}^{\infty} \psi_{0,0}(\theta, u) \ du \). For small times, \( P(\theta, t) \) retains its initial gaussian shape, with its amplitude decreasing exponentially.
D. Long time regime

In this subsection we determine the long time asymptotic behavior of \( W(\theta, u, t) \), utilizing some of the results obtained in the appendix for arbitrary times. In particular, we adapt the kernel expansion of Eq. (A13) and Eq. (A14) to the long time regime. Differentiating Eq. (A16) with respect to \( t \) and with the gaussian choice for \( \Gamma(\theta) \) we obtain:

\[
\frac{\partial W}{\partial t} = -\int d\theta' du' \psi_{0,0}^{-1}(\theta', u') \Gamma(\theta') + \int_0^t dt' \frac{\partial K}{\partial t'}(\theta, \theta', u, u', t') W(\theta', u', t-t'),
\]

where the integrals in \( \theta' \) and in \( u \) range from \(-\infty\) to \(+\infty\). The time-derivative of the kernel in the last integral can be obtained with the use of the expression obtained in Eq. (A10) but with the summation restricted to non-zero values of the integers \( m \) and \( n \). The contribution to the kernel of the term associated with \( m = n = 0 \) is time-independent, and it has the form \( \psi_0(\theta, u) \psi_0(\theta', u') \). We then replace \( \partial_t K \) with \( \partial_t K' \) where \( K' \) is defined as the kernel without the first \( (m, n = 0) \) summand.

The function \( K' \) and its time derivative contain exponentially vanishing terms in \( t \). The time integrand in Eq. (21) will therefore be appreciable only for \( t' \leq \Omega_c^{-1} \) where \( \Omega_c \) is a cutoff frequency of the order of \(|\lambda_{1,0}| = \Omega \). For \( t \gg \Omega_c^{-1} \) we can approximate \( W(\theta', u', t-t') \approx W(\theta', u', t) \) and restrict the time interval from the origin to \( \Omega_c^{-1} \). Integrating by parts, and using the above approximation for \( W(\theta', u', t) \), the time integrals yield:

\[
\frac{\partial W}{\partial t} = -\int d\theta' du' \psi_{0,0}^{-1}(\theta', u') \Gamma(\theta') + \left\{ W(\theta', u', t) \left[ K(\theta, \theta', u, u', 0) + K'(\theta, \theta', u, u', \Omega_c^{-1}) - K'(\theta, \theta', u, u', 0) \right] \right\}.
\]

This equality is simplified by \( K'(\theta, \theta', u, u', \Omega_c^{-1}) \) being negligible. We can now rewrite the right hand side of Eq. (22) as:

\[
\frac{\partial W}{\partial t} = -\int d\theta' du' \left[ \psi_{0,0}^{-1}(\theta', u') \Gamma(\theta') + \psi_{0,0}(\theta, u) \psi_{0,0}(\theta', u') W(\theta', u', 0) \right] .
\]

Since we are dealing with non-zero times, the \( \theta' \) integration can be performed under the assumption that \( \Gamma(\theta') \) is highly peaked around \( \theta^* \) and \( \Gamma(\theta) \approx \kappa, \delta(\theta - \theta^*) \):

\[
\frac{\partial W}{\partial t} = -\kappa \psi_{0,0}(\theta, u) \int_{-\infty}^{\infty} du' W(\theta^*, u', t).
\]

E. The two time scales

As anticipated, two different scenarios for \( P(\theta^*, t) \) emerge from the analysis carried out in the previous subsections. From Eq. (24), at early times, the decay to the acceptor state is rapid, occurring at a rate \( r_1 = \kappa/\sqrt{2\pi\sigma} \), whereas at latter times the rate is as given above: \( r_2 = \kappa \psi_0(\theta^*) \). The ratio between the two is

\[
\frac{r_1}{r_2} = \sqrt{\frac{k_B T}{\sigma \Omega^2}} \exp \left[ \frac{\Omega^2}{2k_B T} (\theta^*)^2 \right] \gg 1,
\]

as follows from the assumptions made on the gaussian \( \Gamma(\theta) \). The initial decay is much faster than that at later times.

F. Numerical results

Based on the general solution of Eq. (A16), we present a numerical analysis of the distribution function \( W(\theta, u, t) \) for different choices of its arguments. In this equation the probability distribution \( W(\theta, u, t) \) is cast in a Volterra-type formulation, for which solutions can be constructed iteratively in time. The probability distribution \( W(\theta, u, t) \) as expressed in Eq. (A16) in fact, depends only on its previous history and on the known propagator function.

For a numerical approach, it is necessary to discretize the \( \theta, u, t \) variables and keep track of the value of \( W(\theta, u, t) \) for every position and velocity at every temporal iteration. While feasible, this approach is rather cumbersome, since for every time step \( t_k = k \Delta t \) we must create a new \( O(N^2) \) matrix \( W(\theta_i, u_j, t_k) \), \( 1 \leq i, j \leq N \), where \( N \) is the number of spacings for the position and velocity meshes. On the other hand, the evaluation at \( W(\theta^*, u_j, t_k) \) where \( \theta^* \) represents the \( \theta_i \) interval centered on the optimal value \( \theta^* \) is greatly simplified if the corresponding mesh is chosen so that \( \Gamma(\theta) \) may be replaced for all purposes by a delta function at non-zero times. The recursive equations now involve only the \( O(N) \) element vector \( W(\theta^*, u_j, t_k) \), \( 1 \leq j \leq N \).

At \( t = 0 \), when the propagator itself is a point source, the gaussian shape for \( \Gamma(\theta) \) must be retained for finiteness, but the iteration at a time that is far from zero does not involve values of the position that are significantly
different from $\theta^*$. The $u$ mesh is chosen with $\Delta u = 0.05$ and the time interval spacing is $\Delta t = 0.01$.

In order to insure consistency with the constraint $\sqrt{q/\gamma \Omega^2} \ll \theta^*$ we choose the following parameters: $\sigma = 10^{-4}$, $\gamma \Omega^2 = 2q$, $\theta^* = 1.5$. The $\alpha$ parameter for the underdamped case is chosen as $\alpha = 0.02$, whereas $\kappa$ is fixed at $\kappa = 0.4$. The resulting probability distribution $W(\theta^*, u, t)$ is plotted in Figure 2 as a function of $u$ for various time intervals.

Two features of the evolving distribution are noteworthy. The first is the depression around $u = 0$. The second is a clear asymmetry in the velocity distribution, in that the distribution for negative values of the velocity, $u$, is lower than for positive $u$ values. The reason for the first feature is the fact that when the velocity is low, a pair will remain in a nearly optimal configuration longer, and hence a tunneling event, leading to depletion of the distribution, is more likely. The asymmetry can be ascribed to the fact that the optimal orientation is at positive values of the parameter $\theta$. The time evolution equation encapsulates two mechanisms, one pushing the distribution towards its Boltzmann limit, the other being the tunneling process that leads to depletion of the distribution at values of $\theta$ close to $\theta^*$. In light of the trajectory of the underdamped oscillation, a member of the ensemble with negative velocity, $u$, is likely to be within a half an oscillation period of having passed with a small velocity through $\theta^*$, which is positive, while a representative with positive $u$ is more likely to have spent more then half an oscillation period away from the optimal tunneling configuration. This latter, positive $u$ configuration will have had more time to experience the “restorative” effects of the mechanism that acts to generate the Boltzmann distribution.

It is also possible to perform a $u$-variable integration and obtain the time dependence of $P(\theta^*, t)$. The parameters are chosen as above, and the two time scale decay of $P(\theta^*, t)$ can be clearly seen to occur with rates $r_1$ and $r_2$ as described in Eq. (27). Also note that both at large and short times $P(\theta^*, t)$ is proportional to $W(\theta^*, 0, t)$. The above results, and the expressions for $r_1$ and $r_2$ are not affected by changes in the damping variable $\alpha$. As anticipated, Figure 3 clearly shows the double exponential decay of $P(\theta^*, t)$, in agreement with the experimental results of [10, 17].

IV. DISCUSSION

The model we have presented is expected to be of significant relevance to charge transfer in DNA. Thermal fluctuations strongly affect the structure of molecule, and an accurate description requires this motion to be taken into account.

Not only has the existence of fluctuations been experimentally documented [12], but it has also been suggested [13] that the motion that most affects the electronic coupling between base pairs - what we have referred to as

\[ \tau(\theta) - \text{is their sliding one with respect to the other. It must be pointed out that both these studies focus on DNA in solution, not on dry strands of DNA.} \]

On the other hand, charge transport with more than one rate has been reported in the literature [16]. For an oligomer with the ethedium molecule acting as the donor, charge transfer is found to occur along the same patterns as described by our model, with two time scales of 5 and 75 picoseconds. Two-time-scale decays are also observed in a series of measurements [17] performed on shorter strands of donor and acceptor complexes (Ap-G). In these experiments the Ap donor can be treated, for all practical purposes, as an intrinsic purine base, and the ambiguity related to the choice of an extraneous donor (the ethedium of the previous reference) is removed.

In both these experiments, an increase in the length results in a competition between the fast and slow ex-
ponential decays in favor of the slower time component. Increasing the length of the system diminishes the possibility that multiple base pairs simultaneously arrange in the configuration that facilitates rapid charge transfer. When the process of optimal alignment does occur (a relatively likely event only for a few base pairs), the tunneling might not even require localization of the charge on each base pair, and super-exchange can take place.

For long strands of DNA, thus, we expect the two intrinsic rates associated to a single charge transfer to be averaged out in favor of the slower component. Traces of this unusual two time scale migration mechanism however, may be found in the fact that DNA conductivity is enhanced upon increasing the temperature \[32\], presumably allowing for greater base pair motion. Charge transfer is also hindered by disruptions to the stacking, which alter the base pair’s ability to find optimal transfer configurations, such as the insertion of bulges along the helix or of strong mismatches within the base pair stacking \[33, 34\] which are poorly compatible with the intrinsic conformation of the aromatic pairs. Lastly, it is noted that charge transfer effectiveness seems to be inversely proportional to the measured hypochromicity \[35\], a quantity that determines the ordering of base pairs along a certain direction and defined as the reduction of absorption intensity due to interactions between neighboring electric dipoles. From this data it is apparent that the higher the disorder of the system, the more efficient charge transfer is. It would be interesting to see how different solvent environments affect conduction along the molecule in relation to their effect on structural fluctuations. More temperature-dependent experimental measures are desirable as well.

V. CONCLUSIONS

We have presented a model for a spin boson TLS whose tunneling matrix element depends on the structural conformation of the donor with respect to the acceptor. In the limit that the relative geometry between the two fluctuates in time defining the lowest energy scale, we are led to a classical problem, that of a collection of damped harmonic oscillators obeying a modified Fokker-Planck equation. If charge transfer proceeds only for specific orientations of the donor with respect to the acceptors, the resulting rate for charge transfer is divided into a fast component at short times and a subsequent slower one. These results agree with the experimental findings of two-time-scale behavior, with an initial, brief, rapid, exponential decay followed by a much slower, power-law, decay at later times. The long-time asymptotics of this process are those of a random walk.

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APPENDIX A: GENERAL SOLUTION OF THE KRAMERS EQUATION

We shall adopt a Lie-Algebra approach \[37\] to identify a complete set of orthonormal functions that solve the homogeneous problem in the general case of Eq. \[7\], and through them the general solution for the decay equation \[1\] will be found.

Let us look for solutions of the following type, where \(m\) and \(n\) represent non negative integers:

\[\psi_{m,n}(\theta, u, t) = \psi_{m,n}(\theta, u) e^{-\lambda_{m,n} t}.\]  \hspace{1cm} (A1)

Upon insertion of the above expression in Eq. \[1\] a time independent Schrödinger-like equation can be written:

\[-(\lambda_{m+n} + \gamma) \psi_{m,n} = H' \psi_{m,n},\]  \hspace{1cm} (A2)

where:

\[H'(\theta, u) = -p_u^2 + \gamma u p_u + \Omega^2 u p_u - \gamma u p_u,\] \hspace{1cm} (A3)

and the subscripts represent derivatives, \(\partial_u\). As expected, the time independent Boltzmann distribution satisfies the homogeneous equation, as can be verified by direct substitution with \(\lambda_{0,0} = 0\). The physical requirement that solutions must be well behaved as \(t \rightarrow \infty\), i.e. that the \(\lambda_{m,n}\)’s be non negative, suggest that this is the ground state:

\[\psi_{\text{ground}}(\theta, u, t) = \psi_{0,0}(\theta, u).\] \hspace{1cm} (A4)

The other solutions are found by constructing the ladder operators. For the underdamped case, we introduce the \(\alpha\) variable such that \(\cos \alpha = \gamma/(2\omega)\) and impose that \([H', O] = i O\) with \(l\) and \(O\) respectively complex variable and operator to be determined. In practice, the operator \(O\) corresponds to either a raising or a lowering operator. Two sets of solutions exist for the following “quanta” \(l_{1,2}\):

\[l_1 = \Omega e^{-\alpha}, \quad l_2 = \Omega e^{\alpha},\] \hspace{1cm} (A5)
Let us now look for the full solution $R$ for which the associated raising and lowering operators $R_{1,2}$ and $L_{1,2}$ are:

$$R_{1,2} = -p_{\theta} + l_{1,2} p_{u}; \quad (A6)$$

$$L_{1,2} = \Omega^2 \theta + \frac{q}{\gamma} p_{\theta} + l_{1,2} \left( \frac{q}{\gamma} p_{u} + u \right). \quad (A7)$$

The commutation rules for the above operators can be easily derived as:

$$[R_i, R_j] = 0, \quad [L_i, L_j] = 0, \quad [R_i, L_2] = \Omega^2 (e^{-2i\alpha} - 1), \quad \text{(A8)}$$

The raising operators applied to the ground state yield the set of solutions $\psi_{m,n}$ for Eq. (A2) with the associated eigenvalues $\lambda_{m,n}$ as follows:

$$\psi_{m,n}(\theta, u) = R_{2}^{n} R_{1}^{m} \psi_{0,0}(\theta, u), \quad \lambda_{m,n} = m\Omega e^{-i\alpha} + n\Omega e^{i\alpha}. \quad \text{(A10)}$$

It is worth noting that the Hamiltonian $H'$ can also be reformulated as $H' = (2\Omega i \sin \alpha)^{-1}[(L_2 R_2) - (L_1 R_1)].$

In order to construct solutions to the non-homogeneous problem within the Hilbert space spanned by the set of solutions $\{\psi_{m,n}(\theta, u)\}$, it is necessary to determine the orthonormality of these solutions. To this purpose, let us consider the following $\phi_{m,n}(\theta, u) = \{P_{2}^{n} P_{1}^{m} \psi_{0,0}(\theta, u)\}$ where $P_{1,2}$ are operators defined as:

$$P_{1,2} = -p_{\theta} - l_{1,2} p_{u}. \quad \text{(A11)}$$

We can now prove an orthogonal relation between the two sets, using the commutation rules and introducing $\psi_{0,0}^{-1}(\theta, u)$ as a weighting function:

$$\int \int du \, d\theta \, \phi_{m',n'}(\theta, u) \psi_{0,0}^{-1}(\theta, u) \psi_{m,n}(\theta, u) = C_{m,n} \delta_{m',m} \delta_{n,n'}. \quad \text{(A12)}$$

The integration limits are over the entire real axis, both for $\theta$ and $u$. The orthonormal set of eigenfunctions is thus expressed as $\{C_{m,n}^{-1} \phi_{m,n}(\theta, u)\}$, to which we refer as $\{\phi_{m,n}(\theta, u)\}$. The constant of proportionality $C_{m,n}$ is:

$$C_{m,n} = m! \, n! \left( \frac{\gamma \Omega^2}{q} \right)^{m+n} (1 - e^{-2i\alpha})^{m} (1 - e^{2i\alpha})^{n}. \quad \text{(A13)}$$

Let us now look for the full solution $W(\theta, u, t)$ to Eq. (B), posing it in the following form:

$$W(\theta, u, t) = \sum_{m,n} h_{m,n}(t) \psi_{m,n}(\theta, u) e^{-\lambda_{m,n} t}. \quad \text{(A14)}$$

The $h_{m,n}(t)$ functions are to be determined, in analogy to the scattering problem of particles in quantum mechanics. Let us assume that the decay term is introduced at time $t = 0$, and that the initial distribution is the equilibrium solution to the homogeneous problem, i.e. the ground state as expressed in Eq. (B). Inserting Eq. (A14) in Eq. (B) and using the orthonormality relations, it is possible to find time evolution equations for $h_{m,n}(t)$ and to write a recursion formula for the full solution:

$$W(\theta, u, t) = W(\theta, u, 0) - \int_{0}^{t} dt' \int_{-\infty}^{\infty} d\theta' \int_{-\infty}^{\infty} du' \left[ K(\theta, \theta', u, u', t - t') \psi_{0,0}^{-1}(\theta', u') \Gamma(\theta', u', t') \right]. \quad \text{(A15)}$$

Here, we have kept $\Gamma$ a generic function of all variables and the $K$ function is the response kernel of the system:

$$K(\theta, \theta', u, u', t) = \sum_{m,n} \psi_{m,n}(\theta, u) \phi_{m,n}(\theta', u') e^{-\lambda_{m,n} t}. \quad \text{(A16)}$$

The product $W'(\theta, u, t) = K(\theta, \theta', u, u', t) \psi_{0,0}^{-1}(\theta', u')$, is the distribution function for the homogeneous system, under the initial conditions $W'(\theta, u, 0) = \delta(\theta - \theta')\delta(u - u')$. Its asymptotic behavior reduces to the Boltzmann distribution, and apart from from $t = 0$, it is an analytical function in all its variables. The explicit representation of the kernel may be written by inserting the expressions for $\psi_{m,n}(\theta, u)$ and $\phi_{m,n}(\theta, u)$ in Eq. (A14):
In order to keep a lighter notation, we have suppressed the time dependence of the $T(t)$, $G(t)$, $l(t)$, $m(t)$, $n(t)$ functions. They are defined as:

\[ l(t) \sin \alpha = e^{-\Omega t \cos \alpha} \sin(\alpha + \Omega t \sin \alpha) \quad (A19) \]
\[ m(t) \sin \alpha = e^{-\Omega t \cos \alpha} \sin(\Omega t \sin \alpha) \quad (A20) \]
\[ n(t) \sin \alpha = e^{-\Omega t \cos \alpha} \sin(\alpha - \Omega t \sin \alpha) \quad (A21) \]

The functions $T(t)$ and $G(t)$ are combinations of the above:

\[ T(t) = 1 + l(t) - n(t)l(t) - m^2(t) \quad (A22) \]
\[ G(t) = 1 + n(t) - l(t) - n(t)l(t) - m^2(t) \quad (A23) \]

In order to ensure integrability for Eq. (A13), some limitations are posed on the form of the $\Gamma(\theta^*, u, t')$ function. For instance, the seemingly most natural choice, a delta function centered around $\theta^*$, yields a non integrable expression for $W(\theta, u, t)$ at small times, when the kernel is a product of delta functions itself. Instead, the gaussian choice introduced earlier, with its finite $\sigma$, ensures integrability at all time regimes.

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