Random walk models of electron tunneling in a fluctuating medium

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A modified approach to the electron transfer theory in disordered media is discussed by use of continuous time random walk models accounting for medium fluctuations. The models apply to the situations when the bridging medium between the donor and acceptor pair fluctuates changing coupling between intermediate transferring states. Effect of the latter on the long distance electron transfer is discussed pointing out emergence of nonexponential decay kinetics.

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I. INTRODUCTION

Electron transfer (ET) is fundamental in chemistry [1–3] and biology [4], being an integral part of many processes ranging from photosynthesis and oxidative phosphorylation to molecular electronic design. In numerous biological examples of ET reaction, a single electron is tunneling in an inhomogeneous medium over large distances of several angstroms. The intervening medium can be either a protein backbone or a sequence of cofactors embedded in a protein matrix. Due to a large separation between the donor and acceptor, direct electronic coupling between the chromophores is negligible, rendering thus the question on the effect of medium on enhancement of the electronic coupling [5]. A possible realization of the long-distance ET process is a transfer mediated through the medium that acts as a bridge providing virtual states for the tunneling electron [6].

The long distance, nonadiabatic reaction corresponds to a weak electronic coupling T_{DA} between the state of reactant D and product A, which leads to the expression for the rate

$$k_{ET}=\frac{2\pi}{\hbar}T_{DA}^2\mathcal{F}_{\mathrm{FC}}, \tag{1.1}$$

where $\mathcal{F}_{\mathrm{FC}}$ is the Franck-Condon nuclear factor associated with the nuclear modes activation barrier. In a conventional theory the Condon approximation is assumed, i.e., the electronic coupling T_{DA} is viewed as independent of the coordinates of the medium. To account for thermal fluctuations of the bridge or random intervening medium, the electronic coupling has to be a function of the modes of the medium. The simplest expression that can be proposed in such a case is the Mc Connell formula [6,7]

$$T_{DA}=-\sum_{ij}\beta_{Di}[\mathbf{G}_{bb}]_{ij}\beta_{jA}, \tag{1.2}$$

where the bracketed expression stands for the Green function of the bridge

$$\mathbf{G}_{bb}(\epsilon)=(\mathbf{H}_{bridge}-\epsilon)^{-1}, \tag{1.3}$$

with $\mathbf{H}_{bridge}$ given by the ''tight binding Hamiltonian,''

$$H_{bridge}^{mn}=\epsilon_b\delta_{mn}+\beta(\delta_{m,n+1}+\delta_{m,n-1}). \tag{1.4}$$

This picture represents the limit of the effective ''two-state'' approximation to ET, in which the ''bridge'' should be understood as the tunneling medium (it may consist, e.g., of protein, protein and water, or protein and cofactors [5]). β_{Di} and β_{jA} denote the electronic couplings between the states $|D\rangle(|A\rangle)$ and the states of the bridge, β_{ij} are the couplings between directly overlapping atomic orbitals of neighboring atoms along the tunneling path. For a simplified case of a linear bridge of L orbitals the Green function of the bridge, and in consequence the tunneling matrix T_{DA} is proportional to

$$T_{DA}\approx\prod_j^L\frac{\beta_{j,j+1}}{\epsilon-\epsilon_j}, \tag{1.5}$$

where $\epsilon-\epsilon_j$ is the energy difference between the tunneling energy and the energy of the bridging orbital j. The above formula constitutes the essential part of the ET pathways models [5,7] in proteins, where the calculation of the effective electronic coupling is based on a general assumption that the electron wave function decay is softer for propagating through a chemical bond than through space jump. Since the coupling coefficients β are exponentially decaying function of the distance between subsequent medium centers (atoms), the effective tunneling matrix can be recast in the form

$$\begin{aligned}T_{DA}(x)&=T_{DA}^0\prod_j^L\exp(-\alpha_j x_j)\\&=T_{DA}^0\exp\left(-\sum_j^L\alpha_j x_j\right),\end{aligned} \tag{1.6}$$

where x_j are fluctuations of the atomic coordinates of the bridge, α_j are constants characterizing strength of the coupling to a particular bridge mode j and T_{DA}^0 corresponds to the average, equilibrium tunneling matrix. The sum in the formula above may be viewed as a superposition of random impulses arriving at random instants of time. The length of the electron path between the donor and acceptor reached by time t is then a cummulative sum of virtual jumps $X_j=\alpha_j x_j$ where $L=L(t)$ denotes a process determining the to-

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tal number of random jumps X_j in time interval t. Such a representation of the effective tunneling matrix T^0_{DA} enables us to use the notion of the continuous time random walk (CTRW) as a very convenient mathematical tool to analyze the decay with time of the donor state occupation density.

In this paper we present several stochastic schemes of CTRWs that may induce the empirical time dependence of the average transfer matrix. We discuss an approach based directly on the definition of the distance $X(t)$ reached up by the electron in time interval t. We analyze the statistical properties of counting processes $L(t)$ and jumps X_j yielding in the long time limit the ''classical'' exponential, the stretched exponential and also the power-tailed decays with time. Our analysis of a class of nonexponential decays is based on the idea of negative-binomial-stable distributions [8–10].

II. RANDOM WALK MODEL OF THE TUNNELING PATH

The continuous (fractal) time random walk, a walk with random waiting times between successive jumps, introduced by Montroll and Weiss [11] has been successfully applied, for instance, to fully developed turbulence, transport in disordered or fractal media, intermittent chaotic systems, and relaxation phenomena [12–16]. The common feature of these applications is that they exhibit anomalous diffusion. It is manifested by a non-Gaussian asymptotic distribution (propagator, diffusion front) of distance reached up to large time t by a walker initially at the origin. The analysis of the asymptotic distribution in most approaches is based on a formal expression for the Fourier-Laplace transform of the total distance and hence the useful, explicit inversion formulas have been provided only under some restrictive assumptions on spatiotemporal coupling. In general, the single jump of the electron along the tunneling path between the donor and acceptor depends on its waiting time in an arbitrary way, yielding both decoupled and a class of various coupled memory CTRWs. The purpose of this paper is to consider the distribution of the resultant 1-dim hopping when the steps occurring in subsequent jumps fluctuate in number and when the length of each step is governed by the distributions that are asymptotic to stable distributions, i.e., those that remain invariant under convolution operation. The advantage of such an approach is that rigorous results can be derived without specifying the character of spatiotemporal coupling and with a limited knowledge of accurate statistics of the jumps' lengths.

Let us first discuss the exponential decay of the average transfer matrix. It might be connected to the following stochastic scenario. Assume that the total number $L(t)$ of virtual jumps exerted in time t by an electron on its path between the donor and acceptor is described by the Poisson counting process with the intensity $\nu(t)$. This assumption is equivalent to the fact that the total path of the electron is a superposition of random ''impulses'' arriving at random Poisson times. The total length $X(t)$ of the electron path is then a cumulative sum

$$X(t)=\sum_{j=1}^{L(t)} \alpha_j x_j, \tag{2.1}$$

where $X_j=\alpha_j x_j$ are assumed in the form of nonnegative independent and identically distributed (IID) random variables. In such an approximation the path length is described as a linear Markov ''birth process'' [17–19]. The probability distribution of the dominant path length

$$p(x,t)=\frac{d\,\mathrm{Prob}[X(t)\leqslant x]}{dx}, \tag{2.2}$$

can be evaluated by using the technique of the characteristic function

$$\phi(s)=E[e^{isX}]=\sum_{j=0}^{\infty} E[e^{isX}|L(t)=j]\mathrm{Prob}[L(t)=j]. \tag{2.3}$$

Due to the independence of variables X_j, the conditional expectation value in the formula above can be represented in the form

$$\phi(s)=E[e^{isX}]=e^{-\nu(t)}\sum_{j=0}^{\infty}[\phi_X(s)]^j\frac{[\nu(t)]^j}{j!}. \tag{2.4}$$

For nonnegative X_j distributed exponentially $p_X=\beta e^{-\beta X}$ with $\beta>0$ that leads to

$$\phi(s)=e^{-\nu(t)}\sum_{j=0}^{\infty}\left(\frac{\beta}{\beta-is}\right)^j\frac{[\nu(t)]^j}{j!}, \tag{2.5}$$

from which the desired probability density follows as the inverse Fourier transform

$$\begin{aligned} p(x,t)&=e^{-\nu(t)-\beta x}\sum_{j=0}^{\infty}\frac{[\beta\nu(t)]^{j+1}x^j}{(j+1)!j!}\\ &=e^{-\nu(t)-\beta x}\left(\frac{\beta\nu(t)}{x}\right)^{1/2}J_1(2\sqrt{x\beta\nu(t)}), \end{aligned} \tag{2.6}$$

where $J_1(z)$ is the modified Bessel function of the first kind. The mean value and the variance of the dominant path can be obtained directly from the characteristic function

$$E[X(t)]=\nu(t)\beta^{-1},\quad \sigma^2(t)=2\nu(t)\beta^{-2}, \tag{2.7}$$

which gives also an estimate for the average transfer matrix T_{DA},

$$\begin{aligned} E[T_{DA}]&=T^0_{DA}e^{-\nu(t)}\sum_{j=0}^{\infty}\left(\frac{\beta}{\beta+1}\right)^j\frac{[\nu(t)]^j}{j!}\\ &=T^0_{DA}e^{-\nu(t)[1/(1+\beta)]}. \end{aligned} \tag{2.8}$$

Time dependence of the average transfer matrix is then fully determined by the intensity $\nu(t)$. For constant frequency $\nu(t)=\nu t$, the decay of the transfer matrix over long distance of ET reaction is governed by a characteristic time $(1+\beta)/\nu$.

Let us now discuss the nonexponential decays. We provide calculations carried out for the average transfer matrix based on limit theorems for sums of a random number of

nonnegative IID random variables. In this case the limiting probability distributions of $X(t)$ for large t can be represented via stable laws [20]. To describe the electron path we use, in analogy to the geostable distribution [21], the notion of the negative-binomial-stable distributions [8,9].

III. LIMITING DISTRIBUTIONS FOR BINOMIAL RANDOM WALKS

This section discusses properties of one-dimensional random walks with fluctuating step number that follows statistics of the negative binomial distribution. By assuming the model in which $L(t)$ follows the negative binomial law, we allow for the clustering in the number of random steps. This can be shown by noticing that the negative-binomial law can be obtained as a result of mixing a Poisson distribution with a gamma distribution

$$\mathrm{Prob}\{L(t)=l\}=\int_0^\infty \frac{(\nu t)^l e^{-\nu t}}{l!} f(\nu)\, d\nu, \tag{3.1}$$

where $f(\nu)$ is given by

$$f(\nu)=\frac{c^r}{\Gamma(r)} e^{-c\nu}\nu^{r-1}. \tag{3.2}$$

As an effect of mixing, random variable $L(t)$ is distributed according to

$$\begin{aligned}\mathrm{Prob}\{L(t)=l\}&=\frac{\Gamma(l+r)}{\Gamma(r)l!}\left(\frac{c}{c+t}\right)^r\left(\frac{t}{c+t}\right)^l\\&=\frac{\Gamma(l+r)}{\Gamma(r)l!}p^r(1-p)^l.\end{aligned} \tag{3.3}$$

The distribution of intervals between the random points governed by the negative-binomial law Eq. (3.3) is

$$\begin{aligned}\mathrm{Prob}\{l(t_0,t)\geqslant 1\}&=1-\mathrm{Prob}\{l(t_0,t)=0\}\\&=1-\left(\frac{c}{c+t}\right)^r,\end{aligned} \tag{3.4}$$

from which the probability density follows by differentiation. In contrast to the simple Poisson case when the distances between randomly occurring points are exponentially distributed random variables, the negative-binomial point process leads to the Pareto distribution of intervals,

$$\begin{aligned}T(t)&=\frac{\mathrm{Prob}\{l(t_0,t)\geqslant 1\}}{dt}\\&=c^r r(c+t)^{-r-1}.\end{aligned} \tag{3.5}$$

The moment-generating function for the negative-binomial distribution

$$\begin{aligned}\phi(z)_{NB}&=E[z^r]=\sum_{i=1}^{\infty} p_i z^i\\&=\frac{p^r}{(1-qz)^r},\quad z=e^{is},\end{aligned} \tag{3.6}$$

is fully characterized by the parameters p and r [$q=1-p$, for the particular case of negative-binomial statistics represented by Eq. (3.3), $p=c/(t+c)$] from which, for $z=1$ the first two moments may be found by differentiating

$$E[L]=\frac{r(1-p)}{p},\quad \sigma^2[L]=\frac{r(1-p)}{p^2}. \tag{3.7}$$

The simplest statistical model leading to a negative-binomial number fluctuations of the path steps L is a birth-death-immigration model for the formation of subsequent joints in the L chain [18]

$$\begin{aligned}\frac{dP_l}{dt}&=\mu(l+1)P_{l+1}-[(\lambda+\mu)l+\theta]P_l\\&\quad+[\lambda(l-1)+\theta]P_{l-1},\end{aligned} \tag{3.8}$$

where $P_l(t)$ is the probability of finding l joints at time t, λ, and μ are, respectively, the birth and death rates for creation (annihilation) of the joint per unit of time and θ stands for the constant production of joints indepenent of their actual number. Equation (3.8) can be solved exactly by use of the generating function $\phi(z,t)$, which along with the initial condition $L(0)=0$ leads to

$$\phi(z,t)=\left(\frac{\lambda-\mu}{\lambda e^{(\lambda-\mu)t}-\mu}\right)^{\theta/\lambda}\left[1-z\frac{\lambda e^{(\lambda-\mu)t}-\lambda}{\lambda e^{(\lambda-\mu)t}-\mu}\right]^{-\theta/\lambda}. \tag{3.9}$$

The above expression is exactly of the type Eq. (3.6) and defines negative-binomial distribution for $P(l,t)$ with parameters $p=(\lambda-\mu)(\lambda e^{(\lambda-\mu)t}-\mu)^{-1}$ and $r=\theta/\lambda$. The class of negative-binomial distributions has a long-time tradition in biological [18,19] and physical [22] modelling. In biology overdispersed negative-binomial distribution (relative variance for the latter is $1/p$ and thus always $\geqslant 1$) has been applied to model growth of populations; physical examples [22] cover among others, random walk models of the scattered electromagnetic field in granular materials.

Negative-binomial step number fluctuations introduce correlations into the random walk [cf., Eq. (3.5)] that are characterized by clustering of subsequent steps. That result can be further generalized by considering nonhomogeneous or nonstationary Poisson process for which $\nu(t)$ varies with time.

Let the number $L(t)$ of virtual jumps of an electron (or the number of connections forming the tunneling path) at time t be distributed according to the negative-binomial law obtained by mixing a nonstationary Poisson process with parameter $\nu(t)=\nu t^\alpha$ with the gamma density (3.2). The resulting distribution adopts the form

$$\mathrm{Prob}\{L(t)=l\}=\frac{\Gamma(l+r)}{\Gamma(r)l!}\left(\frac{c}{c+t^{\alpha}}\right)^{r}\left(\frac{t^{\alpha}}{c+t^{\alpha}}\right)^{l}. \quad (3.10)$$

In terms of the above interpretation, clustering parameter r is expressed by the ratio between frequencies of free creation of joints and the production of new bonds out of existing ones.

We will further focus on limiting forms of the probability density functions for the variable $X(t)$ being the length of the path created out of $L(t)=l$ random elements. The counting process $L(t)$ is taken as independent of jumps X_j, which are assumed to form a sequence of nonnegative IID random variables belonging to the domain of attraction of the completely asymmetric Lévy-stable law $S_{\beta,1}$ [20], i.e.,

$$\mathrm{Prob}\{X_j>x\}=Bx^{-\beta}, \quad (3.11)$$

or

$$\lim_{n\to\infty}\frac{\sum_{j=1}^{n}X_j}{[\Gamma(1-\beta)]^{1/\beta}n^{1/\beta}}=B^{1/\beta}S_{\beta,1}, \quad (3.12)$$

for large x and $0<\beta<1$. A power law distribution Eq. (3.12) would indicate here that no matter the scale at which one is looking at the distribution of lengths X_i, the same proportion of smaller and larger contributions X_i's to the electron path is detected.

For this model of decoupled random walk, as t tends to infinity, the limiting distribution of the number of jumps l converges to a gamma distribution

$$\lim_{t\to\infty}\mathrm{Prob}\left\{\frac{L(t)}{t^{\alpha}}\leqslant l\right\}\to\frac{1}{c}G_{r,1}(l). \quad (3.13)$$

In fact, from Eq. (3.6) one gets

$$\begin{aligned}\Phi_{NB}(s)&=\left\{\frac{(c+t^{\alpha})}{c}\left[1-\left(1-\frac{c}{c+t^{\alpha}}\right)\exp\left(\frac{is}{t^{\alpha}}\right)\right]\right\}^{-r}\\&\to\left[\left(1-i\frac{s}{c}\right)\right]^{-r}\\&=E\left[\exp\left(i\frac{s}{c}G_{r,1}\right)\right], \quad (3.14)\end{aligned}$$

where $(1/c)G_{r,1}$ stands for the gamma random variable whose distribution density function is given by

$$g(x)=[c^{r}\Gamma(r)]^{-1}x^{r-1}e^{-cx}, \quad x>0. \quad (3.15)$$

Accordingly, the long time limit ([9,10]) for the length of the path traversed by an electron tends to

$$\lim_{t\to\infty}\mathrm{Prob}\left\{\frac{X(t)}{At^{\alpha/\beta}}<x\right\}\to V(x), \quad (3.16)$$

where $A=[\Gamma(1-\beta)]^{1/\beta}]>0$ is a normalizing constant and $V(x)$,

$$V(x)=\mathrm{Prob}\left\{\left(\frac{B}{c}G_{r,1}\right)^{1/\beta}\leqslant l\right\}, \quad (3.17)$$

represents the distribution of a random variable V given by the formula

$$V=\left(\frac{B}{c}G_{r,1}\right)^{1/\beta}S_{\beta,1}. \quad (3.18)$$

The random position of the electron for long times (large t) can be hence expressed as

$$X(t)=At^{\alpha/\beta}\left(\frac{B}{c}G_{r,1}\right)^{1/\beta}S_{\beta,1}. \quad (3.19)$$

In consequence, the time dependence of the transfer matrix T_{DA} average is given by the weighted average of the above random variable, i.e.,

$$E[T_{DA}]=T_{DA}^{0}E\left\{\exp\left[-At^{\alpha/\beta}\left(\frac{B}{c}G_{r,1}\right)^{1/\beta}S_{\beta,1}\right]\right\}. \quad (3.20)$$

Taking into account that the Laplace transform for the stable distribution is [20]

$$E[e^{-uS_{\beta,1}}]=e^{-u^{\beta}}, \quad (3.21)$$

we get

$$\begin{aligned}E[T_{DA}]&=T_{DA}^{0}\int_{0}^{\infty}\exp\left\{-\left[At^{\alpha/\beta}\left(\frac{B}{c}\right)^{1/\beta}x^{1/\beta}\right]^{\beta}\right\}g_{r}(x)dx\\&=T_{DA}^{0}\left(1+\frac{B}{c}A^{\beta}t^{\alpha}\right)^{-r}=T_{DA}^{0}\left(1+\frac{B}{c}\Gamma(1-\beta)t^{\alpha}\right)^{-r}. \quad (3.22)\end{aligned}$$

Let us observe that for $0<\alpha<1$ and $r>0$ the above formula determines the power-tailed long time decay of the average transfer matrix

$$E[T_{DA}]=T_{DA}^{0}(Dt)^{-\alpha r}, \quad D=\left(\frac{B\Gamma(1-\beta)}{c}\right)^{1/\alpha}, \quad (3.23)$$

while for r tending to infinity, $B=1/r$ and any time t, it determines the stretched exponential decay behavior

$$E[T_{DA}]=T_{DA}^{0}e^{-(1/c)\Gamma(1-\beta)t^{\alpha}}, \quad (3.24)$$

with the special case of classical exponential decay as α tends to one. Thus depending on the asymptotic behavior of the distribution of jumps length and properties of the point (counting) process, this simple random walk model qualitatively demonstrates transitions among different regimes of the characteristic decay of an averaged transfer matrix.

From a physical perspective, our approach is similar to the pathway method [5] used in the description of the electron tunneling in biological media. The original formulation of the pathway model, however, focuses severe limitation: it does not include possibility of interference among various paths and the paths for ET transfer are treated as rigid crystallographic structure without accounting for dynamic motion within bridging path. On the other hand, the dynamical motion of the bridge changes its geometry that results in time variations of the orbital overlaps and couplings, giving rise to conformational sensitivity of the Green function Eq. (1.3) and T_{DA}. In this context, it is possible that interference of various contributing paths can dominate the ET mechanism [23], which then becomes controlled by dynamic variations of the intervening medium.

IV. CONCLUSIONS

The long-range transfer of an electron in polymeric or various biological materials is determined by the nature of electronic coupling, which for the long distances is mediated by sequential overlaps of atomic orbitals of the donor, the intervening medium (bridge), and the orbitals of the acceptor. Internal random motion of the medium may result in fluctuations of the tunneling barriers between subsequent transfer states and modulate the electronic coupling. It should be stressed that, those effects are formally due to the dependence of the electronic coupling on the nuclear coordinates of the medium and as such, they express possible deviation from the usual Condon approximation [1,7]. The effects arising from the static and dynamic fluctuations in electronic coupling have been discussed in a number of papers (Refs. [7,23,24] and references therein) related to the electron transport in proteins and polymers. All of them have claimed existence of nontrivial effective coupling resulting from averaging over environmental disorder.

In this paper we have proposed a model to account for fluctuations in long distance electron transfer reaction. Our approach relates to the situation of decoherent transport when the hopping behavior of the transmitted charge can decay slowly with distance. The model is based on CTRW kinetics in the representation of random sums of IID elements that are deviations from equilibrium of the atomic coordinates of the bridging medium. In contrast to other work [13,15], the present approach is based on renewal theory and uses limit theorems for random sums [9,10] of jumps instead of Tauberian theorems for the two-dimensional Laplace-Fourier transform.

The asymptotic average character of the electronic matrix elements has been investigated pointing out that the decay of the electron tunneling can exhibit nonexponential behavior similar to anomalous relaxation in complex glasslike systems.

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