Fractional electron transfer kinetics and a quantum breaking of ergodicity

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Dissipative curve-crossing problem provides a paradigm for electron-transfer (ET) processes in condensed media. It establishes the simplest conceptual test bed to study the influence of the medium’s dynamics on ET kinetics both on the ensemble level, and on the level of single particles. Single electron description is particularly important for nanoscaled systems like proteins, or molecular wires. Especially insightful is this framework in the semi-classical limit, where the environment can be treated classically and an exact analytical treatment becomes feasible. Slow medium’s dynamics is capable to enslave ET and bring it on the ensemble level from a quantum regime of non-adiabatic tunneling to the classical adiabatic regime, where electrons just follow to the nuclei rearrangements. This classical adiabatic textbook picture contradicts, however, in a very spectacular fashion to the statistics of single electron transitions, even in the Debye, memoryless media, named also Ohmic in the parlance of the famed spin-boson model. On the single particle level, ET remains always quantum and this was named a quantum breaking of ergodicity in the adiabatic ET regime. What happens in the case of subdiffusive, fractional, or sub-Ohmic medium’s dynamics, which is featured by power law decaying dynamical memory effects typical e.g. for protein macromolecules, and other viscoelastic media? Such a memory is vividly manifested by anomalous Cole-Cole dielectric response typical for such media. This is the question which is addressed in this work based both on precise numerics and an analytical theory. The ensemble theory remarkably agrees with the numerical dynamics of electronic populations, revealing a power law relaxation tail even in a deeply non-adiabatic electron transfer regime. In other words, ET in such media displays clearly a fractional kinetics. However, a profound difference with the numerically accurate results occurs for the distribution of residence times in the electronic states, both on the ensemble level and on the level of single trajectories. Ergodicity is broken dynamically even in a more spectacular way than in the memoryless case. Our result question the applicability of all the existing and widely accepted ensemble theories of electron transfer in fractional, sub-Ohmic environments, on the level of single molecules, and provide a real challenge to face, both for theorists and experimentalists.

I. INTRODUCTION

Electron transfer (ET) is an important physical phenomenon across many research areas ranging from meso- and nanoscale physics, including physics of quantum dots, to molecular and chemical physics, as well biophysics \[1,6\]. It is central e.g. for bioenergetics \[6,10\]. On nanoscale, the single-electron transfer is especially important and relevant, and the dynamics of the reaction coordinate coupled to ET often cannot be disregarded even for a long-range ET in proteins \[11\]. Electron as a light particle is fundamentally quantum in its properties even if, e.g., theory of adiabatic electron transport can be formulated as a purely classical theory on the ensemble level \[1,2,3,7,8\]. A common rationale behind this is that in such a regime electrons just follow adiabatically to the nuclear rearrangements, and nuclei can often be treated classically at sufficiently high temperatures \[1,2,3,7,8\]. This classical point of view has recently been challenged on the level of a single trajectory description by showing that the statistics of single-electron transitions between two diabatic quantum states is fundamentally different from the results of the classical theory of adiabatic ET \[12,13\]. The reason for this lies in a fundamentally quantum nature of electron transitions, even in the adiabatic transport regime \[12\]. Hence, we are dealing with a truly quantum breaking of ergodicity in a seemingly classical adiabatic regime. This phenomenon should be distinguished from other non-ergodic effects caused by slow relaxation modes of the environment (classical breaking of ergodicity) \[12,13\]. In this respect, it is worth stressing that we mean here the genuine dynamical non-ergodic effects, entering through a relativley slow dynamics of the reaction coordinate coupled to the electron transfer, rather than via a non-ergodic change of the medium’s reorganization energy in polar solvents \[16,18\]. The latter one can also be an important issue per se. However, it is beyond the scope of this work dealing with a one-dimensional reaction coordinate description, as the simplest pertinent dynamical model \[19,23\]. All the rest degrees of environment are not coupled directly to the electron transfer dynamics and act as a memory friction and the corresponding correlated thermal noise affecting the dynamics of the reaction coordinate. This leads ultimately to a breakdown of the rate description. The environment is assumed to be at thermal equilibrium, obeying the fluctuation-dissipation theorem (FDT) \[24,25\]. Here lies a fundamental difference with Refs. \[16,18\]. However, our description can also be easily generalized to account for nonequilibrium noise or periodic field, produced either externally, or

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(noise) as a result of nonequilibrium conformational dynamics [22, 26, 32], as in various molecular machines [33], including electron tunneling pumps [32, 34]. One should also mention a general notion of ergodicity in the theory of stochastic processes [35]. Namely, it concerns coincidence of single-trajectory time-averages over a very large (infinite in the theory) time interval and the (infinite in the theory) ensemble averages for the same process. The ergodicity in question can be defined and understood in various senses, e.g. in the mean value (mostly commonly used in statistical physics), in the variance of random processes [35]. Whenever the ensemble and trajectory averages are different, we are speaking about a broken ergodicity. In this work, we understand ergodicity in a kinetic sense [18, 36]. Namely, if an equilibrium ensemble theory is capable to describe statistics of multiple subsequent single-electron transitions, revealed e.g. in a very long “on-off” blinking recording [37, 38], the ergodicity in this kinetic sense holds, and, otherwise, it does not. Our major focus in this paper is on what happens when quantum and classical dynamical breaking of ergodicity meet in anomalous, non-exponential ET transport kinetics, which cannot be rigorously characterized by a rate anymore?

We address this fundamental challenge within a dissipative curve-crossing problem [6, 8, 39], with the reaction coordinate treated classically. Here, the Zusman model of electron transfer generalized to non-Debye environments [21, 40], i.e. with the reaction coordinate coupled to a sub-Ohmic bosonic thermal bath [41] instead of the standard Ohmic one [20], provides an ideal playground. This model corresponds to a subdiffusive motion of nuclei on the diabatic curve, corresponding to a particular localized electronic state, which in the case of standard one-dimensional parabolic curves leads to a Mittag-Leffler relaxation of the reaction coordinate, when the inertial effects are neglected [16, 42]. It is initially stretched exponential and then changes to a power law. Such a relaxation behavior corresponds precisely [42] to the Cole-Cole anomalous dielectric response [42], commonly measured in many molecular systems, including proteins, DNAs, cytosol of biological cells, and biological membranes [44]. Even bounded water in many biological tissues displays clearly a Cole-Cole response, unlike the bulk water [44]. Such a slow, non-Debye relaxation seems to immediately imply a classical breaking of ergodicity, even if this fundamental feature does not seem to be realized in the mainstream research on sub-Ohmic spin-boson model. In this respect, it should be mentioned that a standard spin-boson model of electron transfer can be derived from the Hamiltonian corresponding to the Zusman model [20] if to assume that the reaction coordinate equilibrates very fast. However, namely this assumption is not easy to justify for the sub-Ohmic environment. Indeed, the pertinent physical model is one of spin 1/2 (mathematically equivalent to a two-level quantum system) coupled to a harmonic oscillator (reaction coordinate), which in turn is coupled to N thermal bath oscillators modeling the environment. If only the reaction coordinate relaxes infinitely fast with respect to the spin dynamics, it is possible to use a canonical transformation to N + 1 harmonic oscillators at thermal equilibrium, which are directly coupled to the spin, what corresponds to the standard spin-boson model [21]. Otherwise, this is not possible, and if the relaxation becomes asymptotically a power law, the above assumption becomes generally rather questionable indeed.

It must be stressed that the adjective “slow” has always a relative meaning. Perceived absolutely, it can be very misleading. This is so because a typical time constant $\tau_r$ entering the Cole-Cole dielectric response expression, see Eq. (39) below, is for the water bound in various biological tissues in the range of 6.8 – 13.8 ps [44]. For fractional dynamics of various proteins, this time scale can also be in the range of 2 – 40 ps, as shown both in molecular dynamics simulations and experiments [15, 42, 50], probably due to low frequency molecular vibrations and hydrogen bond dynamics, or in the range of nanoseconds [51], due to the amino acid side chain rotations. Water at the protein-solvent interface also exhibits akin anomalous relaxation and dynamics in the range of picoseconds [52], which is clearly fast from the point of view of a common sense and everyday experience. Approximate matching between the time scales of anomalous dynamics of protein and water in the hydration shell agrees with the picture of protein dynamics slaved to fluctuations in the surrounding solvent developed by Frauenfelder et al. [53]. The inverse of $\tau_r$ corresponds to the frequency on which the corresponding medium’s degrees of freedom absorb electromagnetic energy most strongly [44]. Nevertheless, Cole-Cole response corresponds to a power law relaxation of the reaction coordinate on the time scale much larger than $\tau_r$, and this can have dramatic consequences for ET occurring on a much larger time scale. The corresponding dielectrical response should be quite stationary in the lab. The low-frequency vibrational degrees of freedom leading to this anomalous dynamics were named fractons [54, 55], while considering proteins as fractal structures of a finite size at the edge of thermal stability [56, 58], for a fixed macroconformation. However, $\tau_r$ can also belong to a many orders of magnitude larger time scale, be in the range of seconds, which was also found experimentally for the slow conformational dynamics of proteins [59, 60]. In fact, $\tau_r$ can span a huge range of variations. Interestingly, even coupling to high-frequency quantum vibrational modes of electron-transferring proteins can exhibit slow power-law distributed “on-off” fluctuations on the time scale from seconds to minutes [61]. In this work, however, we are more interested in the relatively fast, yet anomalous dynamics with $\tau_r$ in the range from pico- to microseconds.

The generalized Zusman model of electron transfer [21] presents here a very suitable theoretical framework to address the problem of ergodic vs. non-ergodic behavior in a semi-classical regime, with nuclei treated classically. Moreover, a very important parameter regime
of non-adiabatic to solvent controlled adiabatic transfer can be studied within the so-called contact approximation of the curve-crossing problem. Here, the electron tunnel coupling is assumed to be much smaller than the medium’s reorganization energy and smaller than the thermal energy $k_B T$\textsuperscript{[19]}. Nevertheless, it can still be treated non-perturbatively so that the transport becomes independent of the strength of electronic coupling (on the ensemble level), when this coupling becomes sufficiently strong. This is the so-called solvent-controlled adiabatic electron transfer regime. The problem was already studied within a non-Markovian generalization of Zusman model by Tang and Marcus\textsuperscript{[40]} in the context of anomalous blinking statistics of quantum dots\textsuperscript{[47, 48, 62]}, in a model of Davidson-Cole medium\textsuperscript{[63]}. Moreover, it has never been addressed on the level of a single-trajectory description in a rigorous way, i.e. by simulating stochastic trajectories which correspond to such a generalized Zusman model within a trajectory jump-surface analogy\textsuperscript{[13, 64, 65]}.

The major advances of this paper are the following. First, we provide a stochastic trajectory description corresponding to the sub-Ohmic Zusman model in the contact approximation. It goes fundamentally beyond the Zusman model itself, which is formulated in the density language, on the ensemble level, and not on the level of single trajectories. Next, we revisit the Tang-Marcus theory of generalized Zusman equations in the contact approximation and confirm it in some basic detail, while deriving and representing the analytical results in a different and more insightful way. Differently from Tang and Marcus, who considered a Davidson-Cole environment\textsuperscript{[63]}, we consider a truly subdiffusive (generalized) Cole-Cole environment, which allows to obtain several very insightful analytical results beyond\textsuperscript{[40]}. For example, a novel analytical result for the population relaxation is completely confirmed by stochastic numerics, which is a remarkable success. Our results reveal that this relaxation has always a universal power law tail, even in the strictly non-adiabatic electron transfer regime, where the major time-course of relaxation is nearly exponential and described by the Marcus-Levich-Dogonadze (MLD) nonadiabatic rate. An analytical expression is derived for both the weight of this tail and the time point of its origin. Next, we derive also the analytical expressions for the statistics of electron transitions both on the single-trajectory and ensemble levels, which follow from the non-Markovian Zusman equations. As a great surprise, the result for the survival probability of many particles in a fixed electronic state fails completely against numerics beyond a strictly non-adiabatic regime of a vanishingly small electron coupling. The one for single trajectories does not fail so badly. It can agree with numerics for a substantial portion of the initial decay of survival probabilities (up to $90\%$, and even more). Moreover, it predicts the correct mean residence time, which is always finite. However, the correct tail of distribution is very different. The theory based on generalized Zusman equations predicts two different asymptotical power-laws, one on the ensemble level and another one on the level of single trajectories. However, the both tails are indeed stretched exponential, as reliable stochastic numerics reveal. By and large, a stretched exponential, or Weibull distribution typifies residence time distributions within the studied model, and not a power law, by a striking contrast with the non-Markovian ensemble description. The situation here is radically different from the memoryless Ohmic case, where the non-equilibrium ensemble-based theory agrees with stochastic numerics remarkably well\textsuperscript{[13]}. Why non-Markovian Zusman-Tang-Marcus model formulated in the density language, on the ensemble level, deeply fails in this respect is explained and a physically more justified ensemble approach invoking a Markovian multi-dimensional embedding of non-Markovian reaction coordinate dynamics is formulated.

II. MODEL

We start from a standard formulation\textsuperscript{[7, 8]} of the problem of electron transfer between two diabatic, localized electronic states, $i = 1, 2$, with electronic energies $E_i(x) = \kappa(x - x_0 \delta_{i1})^2/2 - \epsilon_0 \delta_{i1}$, that depend in the Born-Oppenheimer approximation on one-dimensional nuclear reaction coordinate $x$, which is considered as one-dimensional. Here, for simplicity, we assume that the electronic curves are parabolic (harmonic approximation for nuclear vibrations) and have the same curvature $\kappa$ (no molecular frequency change upon electron transfer). Furthermore, $\epsilon_0$ is the difference between electron energies at equilibrium positions of nuclei, and $x_0$ is the shift of the reaction coordinate equilibrium position upon an electronic transition. The corresponding medium’s reorganization energy is $\lambda = \kappa x_0^2/2$. The diabatic electron curves cross, $E_i(x) = E_2(x^*)$, at the point, $x^* = x_0(1 - \epsilon_0/\lambda)/2$, where the Born-Oppenheimer approximation is not valid (in the diabatic basis of localized states). In the vicinity of this point, electron transitions take place due to tunnel coupling $V_{\text{tun}}$, which is assumed to be constant (Condon approximation). These are the standard assumptions, which fix a minimal and standard (thus far) model considered in this paper. The Hamiltonian of the model formulated until this point reads $H(x) = E_1(x)|1\rangle\langle 1| + E_2(x)|2\rangle\langle 2| + V_{\text{tun}}(|1\rangle\langle 2| + |2\rangle\langle 1|)$. The dynamics of the reaction coordinate $x$ will be treated classically, like the rest of the molecular degrees of freedom. They are assumed to be at thermal equilibrium and to introduce a correlated noise and a memory friction into the dynamics of the reaction coordinate, see below. Hence, we are dealing with a semi-classical description of ET, where the electron dynamics remains, however, quantum.

Next, the probability of making a tunnel transition or a jump from one electronic curve to another can be described within the Landau-Zener-Stückelberger (LZS)
applied at the crossing point. The LZS result (1) is described by a standard Kubo-Zwanzig generalized theory \[ \mathcal{P}_{LZ}(v) = 1 - \exp \left[ -f(v) \right], \] which is a milestone result in the theory of quantum transport. Here,

\[
f(v) = \frac{2\pi}{\hbar} \frac{|V_{\text{tun}}|^2}{|\partial \Delta E(x_0)/\partial x|_{x=x}},
\]

with \( \Delta E(x) = E_1(x) - E_2(x) = \epsilon_0 - \lambda + 2\lambda x/x_0 \) being the difference of electron energies, and \( v \) the reaction coordinate instant velocity at the crossing point. In the lowest second order approximation in the tunnel coupling, \( P_{LZ}(v) \approx f(v) \). This latter result follows from the Fermi’s Golden Rule quantum transition rate

\[
K(x) = \frac{2\pi}{\hbar} |V_{\text{tun}}|^2 \delta(\Delta E(x)),
\]

applied at the crossing point. The LZS result (1) is a nonperturbative result beyond the Golden Rule.

A. Trajectory description

The dynamics of the reaction coordinate will be described by a standard Kubo-Zwanzig generalized Langevin equation (GLE) \[ \mathcal{H}, \mathcal{F} \]

\[
M \ddot{x} + \int_0^t \eta(t-t') \dot{x}(t') dt' + \frac{\partial E_1(x)}{\partial x} = \xi(t),
\]

which depends on the quantum state \( i \). Here, \( M \) is an effective mass of the reaction coordinate, \( \eta(t) \) is a memory friction kernel, and \( \xi(t) \) is a correlated zero-mean Gaussian thermal noise of the environment at temperature \( T \). It is completely characterized by its autocorrelation function (ACF) that is related to the memory friction by the fluctuation-dissipation relation (FDR) frequently named also the second fluctuation-dissipation theorem (FDT) by Kubo, \( \langle \xi(t) \xi(t') \rangle = k_B T \eta((t-t')) \). This description comes from a multi-dimensional picture of the reaction coordinate, where an effective one-dimensional pathway, parametrized by a generalized coordinate \( x \), between two stable configurations of nuclei corresponding to electronic states can be identified. Then, the rest of the molecular vibrations and possibly also the molecular degrees of freedom of a solvent surrounding the ET molecule, e.g., a protein, serve as a thermal bath for the reaction coordinate. They introduce a friction and a noise, which are related by the FDT, as it follows from the main principles of equilibrium statistical mechanics, and a standard derivation of GLE dynamics from a Hamiltonian model \[ \mathcal{H}, \mathcal{F} \]. In this paper, we neglect to the inertial effects \( M \to 0 \), which corresponds to a singular model of overdamped Brownian motion with formally infinite mean-squared thermal velocity, \( v_T^2 = k_B T/M \to \infty \). As explained in Ref. \[ \mathcal{H}, \mathcal{F} \], within this overdamped approximation, an effective linearization, \( P_{LZ}(v) \approx f(v) \), takes place, in fact, even without making explicitly a lower order expansion in \( V_{\text{tun}} \). In the numerical simulations though, we shall use Eq. (1), to avoid an extra, explicit approximation, and to be more general on the trajectory level of description.

Furthermore, we assume that the memory kernel consists of two parts, \( \eta(t) = 2\eta_0 \delta(t) + \eta_\alpha t^{-\alpha}/\Gamma(1-\alpha) \), \( 0 < \alpha < 1 \), where \( \eta_0 \) is normal Stokes friction coefficient, \( \eta_\alpha \) is anomalous, fractional friction coefficient, and \( \Gamma(z) \) is the well-known gamma-function. The former one corresponds the Ohmic model of thermal bath, where the spectral bath density is linear in frequency \( \omega \), \( J(\omega) \propto \eta_0 \omega \). It corresponds to a standard exponential Debye relaxation of nuclei to equilibrium. And the later one corresponds to a sub-Ohmic model of thermal bath, \( J(\omega) \propto \eta_\alpha \omega^\alpha \). For \( \eta_0 = 0 \), the relaxation dynamics of the reaction coordinate in a fixed electron state is described by the Mittag-Leffler function \[ \mathcal{H}, \mathcal{F} \], \( E_{\alpha}(z) = \sum_0^\infty z^n/\Gamma(1+n\alpha) \), as \( \langle \delta x(t) \rangle = \delta x(0) \theta(t) \), with relaxation function \( \theta(t) = E_\alpha([-t/\tau_\alpha]^\alpha] \), where \( \tau_\alpha = (\eta_\alpha/k_B)^{1/\alpha} \) is an anomalous relaxation constant, and \( \delta x(0) \) is an initial deviation from equilibrium position. \( \tau_\alpha \) will be used as a time scale in our simulations. This model corresponds \[ \mathcal{H}, \mathcal{F} \] to famous Cole-Cole dielectric response \[ \mathcal{H}, \mathcal{F} \] commonly measured, e.g., in proteins and lipid membranes \[ \mathcal{H}, \mathcal{F} \], where the inverse of \( \tau_\alpha \) defines a non-Debye frequency at which the medium most efficiently absorbs electromagnetic energy. With \( \tau_\alpha \) in a huge temporal range from picoseconds \[ \mathcal{H}, \mathcal{F} \] to nanoseconds \[ \mathcal{H}, \mathcal{F} \], and even up to seconds \[ \mathcal{H}, \mathcal{F} \], the corresponding fractional relaxation dynamics is typical for proteins. More generally, we can have, however, a mixture of Ohmic and sub-Ohmic environments. As explained earlier \[ \mathcal{H}, \mathcal{F} \], for \( \eta_0 \) sufficiently small, the relaxation in a parabolic well will be almost indistinguishable from the Mittag-Leffler relaxation, and the corresponding dielectric response will be nearly Cole-Cole. We keep \( \eta_0 \) finite for several reasons. First, it allows to justify overdamped approximation even for \( \alpha < 0.4 \), where it becomes questionable for \( \eta_0 = 0 \). Second, such a normal friction component should be typically present, even when it is not dominant, e.g., for a protein in water solvent, or in cytoplasm with a dominating water content. And the third reason will become clear below.

Notice also that the model considered here differs from one corresponding to the Davidson-Cole dielectric response that was studied by Tang and Marcus \[ \mathcal{H}, \mathcal{F} \]. The Davidson-Cole model does not yield asymptotically subdiffusion. This is not a fractional diffusion model. In fact, subdiffusion exists only on the time scale \( t \ll \tau_\alpha \). The asymptotic behavior in both models is very different. The relaxation function within the Davidson-Cole model reads \( \theta(t) = \Gamma(\alpha, t/\tau_\alpha)/\Gamma(\alpha) \), where \( \Gamma(\alpha, z) \) is incomplete Gamma-function. It decays asymptotically exponentially, \( \delta x(t) \sim \exp(-t/\tau_\alpha)/t^{1-\alpha}, t \gg \tau_\alpha \), even faster than the Debye relaxation function \( \theta(t) = \exp(-t/\tau_\alpha) \).

The corresponding thermal noise \( \xi(t) \) is also splitted in our model into the two parts, \( \xi(t) = \xi_0(t) + \xi_\alpha(t) \),
with \( \langle \xi_0(t)\xi_0(t') \rangle = 2k_B T \delta(t - t') \) and \( \langle \xi_0(t)\xi_0(t') \rangle = k_B T n_0(t - t')/\Gamma(1 - \alpha) \). \( \xi_0(t) \) is a standard white Gaussian noise (time derivative of Wiener process), whereas \( \xi_\alpha(t) \) is a fractional Gaussian noise (time derivative of fractional Brownian motion [74–76]). Using the notation of fractional Caputo derivative, \( \frac{d^n}{dt^n} x(t) := \int_0^t (t - t')^{n-\alpha} \frac{d}{dt} x(t')dt' / \Gamma(1 - \alpha) \) [62], the corresponding GLE can be rewritten in the form of a fractional Langevin equation (FLE) [14, 15, 77–81]

\[
\eta_0 \frac{dx}{dt} + \eta_\alpha \frac{d^n x}{dt^n} + \frac{\partial E_i(x)}{\partial x} = \xi_0(t) + \xi_\alpha(t) .
\]

In numerical simulations, dynamics of the reaction coordinate is propagated in accordance with this equation (its finite-dimensional approximate Markovian embedding, see below) in a fixed electronic state and at each crossing of \( x^* \) a jump into another electron state can occur with the above probability \( P_{i\rightarrow j}(x) \). If an electron transition occurs, \( x \) is further stochastically propagated on the other curve \( E_j(x) \), until the electron jumps back, on so on, for a very long time covering huge many transitions.

### B. Generalized Zusman equations

This trajectory model has for arbitrary \( \eta(t) \) in the overdamped limit of \( M \rightarrow 0 \), a known ensemble counterpart. It is provided by the generalized Zusman equations [21], considered in the contact approximation. Indeed, the overdamped motion of the reaction coordinate in one fixed electronic state is described by the non-Markovian Fokker-Planck equation (NMFPE), \( \dot{p}_i(x,t) = \dot{L}(t)p_i(x,t) \), with a time-dependent Smoluchowski operator [82, 84]

\[
\dot{L}_i(t) = D(t) \frac{\partial}{\partial x} \left[ -\delta E_i(x) \frac{\partial}{\partial x} e^{\delta E_i(x)} \right] = \frac{D(t)}{x_T^2} \left( x - x_0 \delta_{2,i} + x_T^2 \frac{\partial}{\partial x} \right)
\]

\[
:= D(t) \dot{L}_i^{(0)} .
\]

Here, \( \beta = 1/k_B T \) is the inverse temperature, \( x_T^2 = k_B T/\kappa \) is the equilibrium variance of the reaction coordinate distribution in a fixed electronic state, and \( D(t) \) is a time-dependent diffusion coefficient whose time-dependence expresses non-Markovian memory effects. It reads [82, 84]

\[
D(t) = -x_T^2 \frac{d}{dt} \ln \theta(t) ,
\]

where \( \theta(t) \) is the coordinate relaxation function in a fixed electronic state, with the Laplace-transform \( \tilde{\theta}(\kappa) := \int_0^\infty e^{-\kappa t} \theta(t)dt \) reading [15, 42]

\[
\tilde{\theta}(\kappa) = \frac{\tilde{\eta}(s)}{\kappa + s \tilde{\eta}(s)} ,
\]

for arbitrary memory kernel \( \eta(t) \) in Eq. [4] (with \( M = 0 \)). It must be emphasized that such equations are known only for strictly parabolic \( E_i(x) \). The exact form of \( D(t) \) for a non-linear dynamics remains simply unknown. From this already, one can conclude that the trajectory description given above is much more general. It can be readily generalized to a nonlinear dynamics of the reaction coordinate. The solution of NMFPE for some initial \( p_i(x,x_0 =0) = \delta(x-x') \) yields the well-known Green functions [82, 84]

\[
G_i(x,t|x') = \frac{1}{\sqrt{2\pi x_T^2 (1-\theta(t))}} \exp \left[ \frac{(x-x_0\delta_{2,i}+x_T^2\theta(t))^2}{2x_T^2(1-\theta(t))} \right] ,
\]

which play an important role in the theory.

It must be mentioned that any convolution-less NMFPE with a time-dependent \( D(t) \) can also be formally brought into an alternative form [82, 84],

\[
\tilde{\tilde{p}}_i(x,t) = \int_0^t \dot{\dot{L}}_i^{(c)}(t-t')p_i(x,t')dt' ,
\]

\( \dot{\dot{L}}_i^{(c)}(t) = M(t)\dot{L}_i^{(0)} \), with a memory-kernel \( M(t) \) which is very different from \( D(t) \) in Eq. [6] or its time-derivative. One can attempt to find it with the above Green function for \( p_i(x,t) \) in Eq. [10]. This yields an integral equation for \( M(t) \). However, it is not easy to solve. The precise expression for \( M(t) \) is not known, and some proposed approximate forms are actually the source of a profound confusion and mistakes in the literature. For example, for the fractional dynamics in Eq. [5] with \( \eta_\alpha = 0 \), we have \( \theta(t) = E_\alpha[-(t/\tau_\theta)^\alpha] \) and \( D(t) = -x_T^2 \ln E_\alpha[-(t/\tau_\theta)^\alpha]/dt \). The very same relaxation function \( \theta(t) \) follows, however, also from the fractional Fokker-Planck equation (FFPE) [86], which is a sort of equation [10] with a memory function, which is some distribution whose Laplace-transform reads \( M(x) = D_\alpha x^{1-\alpha} \), with fractional diffusion coefficient \( D_\alpha = k_B T/\eta_\alpha \). It cannot be inverted to the time domain as some function, but only in terms of a generalized function or distribution corresponding to the integro-differential operator of the Riemann-Liouville derivative [69]. This FFPE can be expressed either with the Riemann-Liouville fractional derivative in its rhs [80], or with the Caputo fractional derivative in its lhs. Using the Caputo derivative, it reads \( \partial^\alpha p_i(x,t)/\partial t^\alpha = D_\alpha \dot{\dot{L}}_i^{(0)} p_i(x,t) \) [82]. The Green function corresponding to this process in a parabolic potential has been found in Ref. [82], and this is not one in Eq. [6]. It must be emphasized once more that this FFPE is not a FPE counterpart of the FLE. Misleadingly enough, the both fractional FPE descriptions yield the same relaxation function \( \theta(t) \) in the parabolic potential [15]. However, already the corresponding Green functions are very different. Moreover, these two fractional diffusion approaches are profoundly different physically [83]. In particular, there is no, in fact, strictly speaking, a stationary limiting process \( x_{st}(t), t \rightarrow \infty \) within the FFPE description, even if a stationary distribution \( p_i^{(st)}(x) = \lim_{t \rightarrow \infty} p_i(x,t) \) does exist.
Indeed, the formally stationary autocorrelation function of the coordinate, which can be obtained from a two-time aging autocorrelation function in Ref. [89] in the formal limit of infinite aging time, is just a constant. In accordance with the Slutsky theorem this means that the process is not ergodic [35] and implies, inter alia, the death of stationary linear response of such and similar processes to time-periodic fields [13, 80, 84]. It indeed has been explicitly found in the related models of anomalous diffusion [91, 92], as well experimentally [93]. In the studies of stationary non-Markovian stochastic resonance [94, 97] it has also been realized that the condition of finite mean residence times (MRTs) is indispensable to have a finite stationary response. Later on, it has been argued that the random processes with divergent MRTs can respond asymptotically only to akin complex non-ergodic perturbances, giving rise to a theory of complexity matching [98]. This profound non-stationarity, even in a wide sense [35], makes such a FFPE process profoundly non-ergodic, even if it is often referred to as a weakly nonergodic process [99, 100]. The breaking of ergodicity described in this work has anything in common with the principal, fundamental non-ergodicity of the FFPE description and the related processes.

In the following, it suffices to know that such an alternative representation [10] in principle exists also for non-Markovian FPE with a time-dependent \( D(t) \). The exact form of \( M(t) \) will, however, not be required. More precisely, we will use the Laplace-transformed Green-function \( \tilde{G}_{i,2}(x,s|x') \) corresponding to the Smoluchowski operator \( \tilde{L}_{1,2}(t) \) which in terms of the Laplace-transformed operator \( \tilde{L}_{i}^{(c)}(t) \) can be expressed in the operator form as \( \tilde{G}_{i}(s) = [s - \tilde{L}_{i}^{(c)}(s)]^{-1} \). For the analytical theory below it suffices to know that such a convolution presentation exists, in principle.

For the model in Eq. [6], the Laplace-transformed relaxation function reads [70]

\[
\tilde{\theta}(s) = \frac{\tau_0 + \tau_r (s \tau_r)^{\alpha-1}}{s \tau_0 + 1 + (s \tau_r)^{\alpha}}, \tag{11}
\]

where \( \tau_0 = \eta_0/\kappa, \tau_r = (\eta_\alpha/\kappa)^{1/\alpha} \). In a particular case of \( \alpha = 0.5 \), which will be studied numerically in this work, the inversion to the time domain can be easily done. It reads,

\[
\theta(t) = \frac{1}{2} \left( 1 + \frac{1}{\sqrt{1 - 4z}} \right) e^{(1 - \sqrt{1 - 4z})^2 t / (4z^2 \tau_r)} \times \text{erfc} \left[ (1 - \sqrt{1 - 4z}) \sqrt{t / (4z^2 \tau_r)} \right] + \frac{1}{2} \left( 1 - \frac{1}{\sqrt{1 - 4z}} \right) e^{(1 + \sqrt{1 - 4z})^2 t / (4z^2 \tau_r)} \times \text{erfc} \left[ (1 + \sqrt{1 - 4z}) \sqrt{t / (4z^2 \tau_r)} \right], \tag{12}
\]

where \( z = \tau_0/\tau_r \), and erfc is complementary error function. Furthermore, for any \( 0 < \alpha < 1 \), if \( \tau_0 \ll \tau_r \), then relaxation follows approximately

\[
\theta(t) \approx E^{(\alpha)}_1[-(t/\tau_r)^\alpha], \tag{13}
\]

except for a small range of initial times \( t < \tau_0 = z \tau_r \).

Now we are in a position to write down generalized Zusman equations by taking electron tunneling into account, which happens at the curve crossing point \( x^* \). For a joint probability density, \( p_i(x, t) \), of electronic level populations \( i \) and values \( x \) of the reaction coordinate these equations read,

\[
p_1(x, t) = -K(x) [p_1(x, t) - p_2(x, t)] + \tilde{L}_1(t)p_1(x, t),
\]

\[
p_2(x, t) = K(x) [p_1(x, t) - p_2(x, t)] + \tilde{L}_2(t)p_2(x, t), \tag{14}
\]

where \( K(x) \) is the Golden Rule expression in Eq. [4]. It can written as \( K(x) = v_0 \delta(x - x^*) \), with \( v_0 = \pi |V_{\text{tun}}|^2 x_0 / (h \lambda) \) being a tunneling velocity at the crossing point. These are nothing else classical anomalous diffusion-reaction equations with sink terms expressing quantum transitions from one to another electronic state. More rigorously they were derived by Tang [21] from a Hamiltonian model in a series of approximations and applied by Tang and Marcus [40] to study statistics of single-electron transitions in a model of quantum dots. Formally, they look similar to the original, memoryless Zusman equations in the contact approximation [19]. In Eq. [13], the memoryless Smoluchowski operators are replaced by ones with a time-dependent \( D(t) \) that expresses non-Markovian memory effects [22, 54]. Beyond the contact approximation, within the four component Zusman equations, \( K(x) \) is an involved function peaked at \( x^* \) whose explicit expression has been found [22] thus far only for a strictly Markovian Debye model. The equations [13] should be distinguished from the equations of Sumi-Marcus [107] or Agmon-Hopfield [108] models generalized to the case of non-Debye environments [109], which look similar for the case of symmetric electron transfer, \( \epsilon_0 = 0 \). In the generalized Sumi-Marcus model, \( K(x) \) is a non-adiabatic ET rate, like one below in Eq. [29], which is modulated by a slow conformational degree of freedom \( x \), via e.g. modulation of the energy bias, \( \epsilon_0 \to \epsilon_0(x) \). It cannot be approximated by a delta-function, at all. The generalized Sumi-Marcus approach corresponds rather to a slow conformational dynamics modulating non-adiabatic electron transfer via the conformation-dependent activation energies \( E^{(\alpha)}_1(x) \). Likewise, slow fractional conformational dynamics can affect the effective tunnel coupling [59, 110] leading also to a slowly fluctuating non-adiabatic rate. Similar approaches have also been developed within a stochastically driven spin-boson model [28, 57, 59, 111]. In the considered case, \( E^{(\alpha)}_1(x) \) and \( V_{\text{tun}} \) are constant. Below we solve equations [14] and compare our solution with the earlier result by Tang. Moreover, our analytical solution will be tested against the numerical results of the stochastic trajectory description. It will be shown where and why the overall approach based on a non-Markovian Fokker-Planck equation fails to describe statistics of single-electron transition events, in principle, i.e. its principal limitations will be revealed. These principal limitations reflect non-ergodic nature of elec-
tron transfer in strongly non-Debye environments.

III. ANALYTICAL THEORY

A. Evolution of electronic populations

Our first goal is to derive an analytical expression for the relaxation of electronic populations \( p_{1,2}(t) = \int_{-\infty}^{\infty} p_{1,2}(x,t)dx \). We start from a formal convolution analogy of Eq. (13) written in the vector-matrix operator form and Laplace-transformed,

\[
[sI + K(x) - \tilde{L}(s)] \tilde{P}(x,s) = P(x,0).
\]  

(15)

Here, \( I \) is 2 \times 2 unity matrix and

\[
\tilde{P}(x,s) = \begin{pmatrix} p_1(x,s) \\ p_2(x,s) \end{pmatrix}, \quad \tilde{L}(s) = \begin{pmatrix} \tilde{L}^{(c)}_1(s) & 0 \\ 0 & \tilde{L}^{(c)}_2(s) \end{pmatrix}, \quad K(x) = K(x) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}, \quad P(x,0) = \begin{pmatrix} p_1(x,0) \\ p_2(x,0) \end{pmatrix}
\]  

(16)

All the corresponding Laplace-transforms are denoted as the original quantities with tilde and Laplace variable \( s \) instead of time variable \( t \). Next, we proceed closely to Ref. 22 and use a projection operator \( \Pi \) whose action on arbitrary function \( f(x) \) is defined as

\[
\Pi f(x) = \begin{pmatrix} p_1^{(eq)}(x) \\ 0 \end{pmatrix} \int_{-\infty}^{\infty} f(x)dx = P_{eq}(x) \int_{-\infty}^{\infty} f(x)dx,
\]  

(17)

where \( p_i^{(eq)}(x) = \exp[-(x-x_0\delta_{i,2})^2/(2x_T^2)]/\sqrt{2\pi x_T^2} \) are the equilibrium distributions of the reaction coordinate in the fixed electronic states. It is easy to check that \( \Pi^2 = \Pi \), and \( \Pi \tilde{P}(x,s) = P_{eq}(x)\tilde{p}(s) \), where \( \tilde{p}(s) = [\tilde{p}_1(s), \tilde{p}_2(s)]^T \) is vector of Laplace-transformed electronic populations. This allows to split \( \tilde{P}(x,s) \) as \( \tilde{P}(x,s) = P_{eq}(x)\tilde{p}(s) + \tilde{P}_1(x,s) \), where \( \tilde{P}_1(x,s) = Q\tilde{P}(x,s) \) is an orthogonal projector and \( Q = I - \Pi \) is a complementary projector, \( \Pi Q = Q \Pi = 0 \). Using standard operations with projection operators and such properties as \( \tilde{L}(s)P_{eq}(x) = 0 \) allows to exclude the irrelevant part \( \tilde{P}_1(x,s) \). After some standard algebra, we obtain the following exact result

\[
[k(s) + sI]\tilde{p}(s) = p(0),
\]  

(18)

with the matrix

\[
k(s) = P^{-1}_{eq} \Pi K \left( I - [sI + Q(K - \tilde{L}(s))]^{-1}QK \right) P_{eq}.
\]  

(19)

This result holds for the class of initial preparations with equilibrated reaction coordinate, \( p_i(x,0) = p_i^{(eq)}(x)p_i(0), \quad p_1(0) + p_2(0) = 1 \). Next, using \( Q\tilde{L}(s) = \tilde{L}(s) \) and formal operator expansions like \( [A + B]^{-1} = [A(1 + A^{-1}B)]^{-1} = [1 + A^{-1}B]^{-1}A^{-1} = \sum_{n=0}^{\infty}(-1)^n(A^{-1}B)^nA^{-1} \), with \( A = sI - \tilde{L}(s), \) and \( B = QK \), the above result can formally exactly be represented as

\[
k(s) = P^{-1}_{eq} \Pi K \left( I - \sum_{n=0}^{\infty}(-1)^n[G(s)QK]^{n+1} \right) P_{eq},
\]  

(20)

where \( G(s) = [sI - \tilde{L}(s)]^{-1} = \delta_{ij}\tilde{G}_i(s) \) is the Laplace-transformed Green function operator. In the coordinate representation, its components read \( \tilde{G}_i(x,s|x') = \delta_{ij}\tilde{G}_i(x,s|x') \), with \( G_i(x,s|x') \) being the Laplace-transformed Green-function in Eq. (9), which is well-known. In this respect, action of operator \( \tilde{G}_i(s) \) on any function \( f(x) \) is defined by the integral \( \int_{-\infty}^{\infty} G_i(x,s|x')f(x')dx' \). Within the considered model with \( K(x) = v_0\delta(x-x^*), \) the multiple integrals entering Eq. (20) can be reduced to powers of one-dimensional integrals and the resulting series can be summed up exactly. We obtain the exact result:

\[
k(s) = \left[ I + K^{(na)}T(s) \right]^{-1}K^{(na)}.
\]  

(21)

Here, the elements of the matrices

\[
K^{(na)} = \begin{pmatrix} k_{11}^{(na)} & -k_{12}^{(na)} \\ -k_{21}^{(na)} & k_{22}^{(na)} \end{pmatrix},
\]  

(22)

are defined via the integral relations

\[
k_{1,2}^{(na)} = \int_{-\infty}^{\infty} K(x)p_{1,2}^{(eq)}(x)dx = \frac{2\pi \tau^{2\nu}_{num}}{h\sqrt{4\pi \lambda k_B T}} e^{-\frac{k_0^{(na)}}{\tau^{2\nu}_{num}}},
\]  

(23)

and

\[
\tilde{t}_{1,2}(s) = \int_{0}^{\infty} dt e^{-st} \left[ G_{1,2}(x^*,t|x^*)/p_{1,2}^{(eq)}(x^*) - 1 \right] = \tilde{G}_{1,2}(x^*,s|x^*)/p_{1,2}^{(eq)}(x^*) - 1/s .
\]  

(24)

Eq. (23) is the celebrated Marcus-Levich-Dogonadze expression \( \frac{E_{1,2}(\nu)}{\tau^{2\nu}_{num}} \) for the rate of non-adiabatic electron transfer. Here, \( E_{1,2}(\nu) = (\nu + \lambda)/4\lambda \) are the activation energies displaying a parabolic dependence on the energy bias \( \epsilon_0 \) (the famous Marcus parabola). The very fact that this is a quantum rate, despite it is often named classical, is expressed by the quantum tunneling prefactor in Eq. (23). Furthermore, the limit \( \lim_{\lambda \rightarrow 0} \tilde{t}_{1,2}(s) = \tau^{ad}_i = 1/k_i^{ad} \), in Eq. (23), when exists, yields the inverse of adiabatic Marcus-Hush \( \frac{E_{1,2}(\nu)}{\tau^{ad}_i} \) rates of electron transfer \( k_i^{ad} \) (for Debye solvents), or their generalizations (beyond Debye...
solvents). As a result, the dynamics of electronic populations is governed by the generalized master equations (GMEs) reading

\[ \dot{p}_1(t) = -\int_0^t k_1(t-t')p_1(t')dt' + \int_0^t k_2(t-t')p_2(t')dt', \]

\[ \dot{p}_2(t) = -\dot{p}_1(t) \]

with the memory kernels defined by their Laplace-transforms

\[ \tilde{k}_i(s) = \frac{k_i^{(na)}}{1 + \tau_1(k_1^{(na)}) + \tau_2(k_2^{(na)})}. \]

This is the first profound result of this work. When exist, the (generalized) Zusman rates of electron transfer read \( k_{1,2} = \tilde{k}_{1,2}(0) \). For example, in the case of Davidson-Cole solvents such rates do exist and a Markovian approximation of the relaxation dynamics can be done on the time scale \( t \gg \tau_1 \). In our case of subdiffusive reaction coordinate, however, \( \lim_{t \to \infty} \tilde{\tau}_i(s) = \infty \), see below, and this has dramatic consequences for ET transfer kinetics is such subdiffusive environments, because a Markovian approximation to \[ 25 \] is generally simply wrong. Namely, in the Appendix A, it is shown that the asymptotic behavior of \( \tilde{\tau}_{1,2}(s) \) for \( 0 < \alpha < 1 \) in the limit \( s \to 0 \) and for sufficiently large activation barriers (over several \( k_B T \)) is

\[ \tilde{\tau}_{1,2}(s) \sim 2r_{1,2}\tau_r(s\tau_r)^{\alpha - 1}, \]

where \( r_{1,2} = E_{1,2}^{(a)}/(k_B T) \) is activation energy in the units of \( k_B T \). On the other hand, the asymptotic behavior of \( \tilde{\tau}_{1,2}(s) \) for large \( s\tau_r \gg 1 \) is

\[ \tilde{\tau}_{1,2}(s) \sim \sqrt{\frac{\eta_0}{\pi}} (e^{r_{1,2}^2} - 1) \tau_r(s\tau_r)^{-1/2}, \]

universally, for any \( \alpha \), whenever \( \eta_0 \neq 0 \). This asymptotics is very important for the statistics of single electron transitions. Here, \( \tilde{\eta}_0 = \eta_0/(\eta_0 \tau_1^{1-\alpha}) = z \) is a scaled normal friction coefficient. By a comparison of \[ 27 \] and \[ 28 \] one can see that the both asymptotics coincide only for \( \alpha = 0.5 \) and for \( \sqrt{\frac{m}{2}} (e^{r_{1,2}^2} - 1) = 2r_{1,2}/\sqrt{\pi} \). Hence, only for a symmetric case, \( r_1 = r_2 = r \) and \( \alpha = 0.5 \) one can choose \( r \) and \( \tilde{\eta}_0 \) so that \[ 27 \] or \[ 28 \] can work approximately uniformly for any \( s \). Fig. \[ 4 \] a, serves to illustrate such a case which offers a possibility for nice analytical expressions, see below. This is actually the third reason for choosing the model with a finite \( \eta_0 \). With \( \eta_0 = 0 \), the large-\( s \) asymptotics of \( \tilde{\tau}_{1,2}(s) \) is

\[ \tilde{\tau}_{1,2}(s) \sim \frac{\Gamma(1 - \alpha/2)\sqrt{\Gamma(1 + \alpha)/2} (e^{r_{1,2}^2} - 1) \tau_r}{(s\tau_r)^{1-\alpha/2}}. \]

In this case, the short and long time asymptotics can never coincide. It will be studied in detail elsewhere.

Furthermore, it is easy to show that the relaxation of populations follows

\[ p_{1,2}(t) = p_{1,2}^{(eq)} + [p_{1,2}(0) - p_{1,2}^{(eq)}]R(t), \]

where \( p_{2,1}^{(eq)} = k_{1,2}^{(na)}/[k_1^{(na)} + k_2^{(na)}] = 1/[1 + \exp(\pm \epsilon_0/(k_B T))] \) are equilibrium populations and \( R(t) \) is a population relaxation function with the Laplace-transform reading

\[ \tilde{R}(s) = \frac{1}{s + k_1(s) + k_2(s)} = \frac{1}{s + k_1^{(na)} + k_2^{(na)}}. \]

This general formal result is equivalent to one obtained by Tang in a different way \[ 21 \], although our notations are very different. Let us consider limiting cases of this expression for the model under study.

1. The limit of solvent-controlled adiabatic transfer

First, we consider the formal limit of \( V_{\text{tun}} \to \infty \), in which we obtain \( \tilde{k}_1(s) \approx k_1^{(ad)}(s) = 1/[\tilde{\tau}_1(s) + \tilde{\tau}_2(s) \exp(-\epsilon_0/(k_B T))] \), \( \tilde{k}_2(s) \approx k_2^{(ad)}(s) = k_1^{(ad)}(s) \exp(-\epsilon_0/(k_B T)) \), and

\[ \tilde{R}(s) = \frac{\tilde{\tau}_1(s)p_2^{(eq)} + \tilde{\tau}_2(s)p_1^{(eq)}}{1 + s[\tilde{\tau}_1(s)p_2^{(eq)} + \tilde{\tau}_2(s)p_1^{(eq)}]}, \]

It must be mentioned once again that physically \( V_{\text{tun}} \) must be much smaller than \( \lambda \) and do not exceed \( k_B T \) in this solved-controlled adiabatic regime. Otherwise, the considered model cannot be physically justified. The result in Eq. \[ 32 \] is the second important result of this paper. In fact, it solves also the problem of overdamped classical anomalous relaxation with arbitrary kernel \( \eta(t) \) in a cusp-like bistable potential consisting of two pieces of parabolas of equal curvature. This is so because in the limit \( \epsilon_0 \to \infty \) the particle crosses the boundary between two domains of attraction with the probability one, once it arrives at the boundary (absorbing boundary). It must be, however, emphasized also that this result does not describe a typical time scale of transitions of single particles between two domains of attraction (which does exist!) because of a broken (!) ergodicity, see below: the ensemble and single-trajectory descriptions are fundamentally different. It describes how the particles redistribute between two attraction domains, all starting e.g. in one of them, whereas approaching an equilibrium distribution (equipartition in the symmetric case). Each particle crosses the boundary huge many times during this equilibration process. An especially insightful and beautiful result is obtained when the both asymptotics, \[ 27 \] and \[ 28 \], coincide. Then, GME \[ 25 \] can approximately be
written as a fractional master equation \[112, 113\]

\[
p_1(t) = -\dot{a}D_t^{-1-\alpha} [k_{\alpha,1}p_1(t) - k_{\alpha,2}p_2(t)] ,
\]

\[
p_2(t) = 1 - p_1(t),
\]

with fractional rates \(k_{\alpha,1} = 1 / [2\tau_r(r_1 + r_2e^{-\epsilon_0/k_BT})]^{\alpha}\)

\(k_{\alpha,2} = k_{\alpha,1}\exp[-\alpha\epsilon_0/k_BT]\)

and fractional Riemann-Liouville time derivative \[69\]

\[
\dot{a}D_t^{-1-\alpha} p(t) := \frac{1}{\Gamma(\alpha)} \frac{d}{dt} \int_0^t \frac{p(t')}{(t-t')^{1+\alpha}} dt'.
\]

This remarkable form, which, anyway, is valid, in fact, only for \(\alpha = 0.5\), the symmetric case, \(\epsilon_0 = 0\) and a special choice of the pair \(\tau_r, r\) (see above), can, however, be misleading. One has to be very careful with it because a perplexed reader might attribute Eq. (33) to a non-stationary CTRW walk with divergent mean residence times in the traps of a rough potential landscape for the reaction coordinate. It corresponds, however, quite on the contrary, to the stationary, equilibrated dynamics of the reaction coordinate. Namely, such surface analogies lead to two very different “fractional” dynamics in the literature, which might look perplexingly very similar \[88\]. In this case, we have

\[
\hat{R}(s) = \frac{\tau_{ad}(s\tau_{ad})^{\alpha-1}}{1 + (s\tau_{ad})^{\alpha}} ,
\]

where we introduced a scaling relaxation constant

\[
\tau_{ad} = \tau_r \left(2r_1p_2^{(eq)} + 2r_2p_1^{(eq)}\right)^{1/\alpha} .
\]

The result in Eq. \[42\] inverted to the time-domain reads \(\hat{R}(t) = E_{\alpha}[-(t/\tau_{ad})^{\alpha}]\), i.e. it is described by the Mittag-Leffler relaxation function, precisely so as the relaxation of the reaction coordinate in the considered Cole-Cole solvent \(\tau_{eq}\), but with a very different scaling time \(\tau_{ad}\). The striking feature is that \(\tau_{ad}\) scales not exponentially with the height of the activation barrier and temperature, but as a power law. For symmetric case,

\[
\tau_{ad} = \tau_r \left(2E^{(a)}/k_BT\right)^{1/\alpha} .
\]

This is a very important result. In the case of rate processes, such power law dependencies are usually attributed to quantum mechanical effects \[41\]. In the present case, however, it has nothing to do with quantum mechanics.

2. Implications for dielectric response

A small digression on linear response should be done here. If to apply a small periodic force \(f(t) = f_0\cos(\Omega t)\) with frequency \(\Omega\) and amplitude \(f_0\) to probe the reaction coordinate in a fixed electronic state, it will respond stationary, in a long-time limit, as \(\langle \delta x(t) \rangle_{\text{eq}} = f_0|\hat{\chi}(\Omega)|\cos(\Omega t - \varphi)\), where \(\hat{\chi}(\omega)\) is a linear response function (LRF) in the frequency domain and \(\varphi = \tan^{-1}\left(\frac{\Im \hat{\chi}(\omega)}{\Re \hat{\chi}(\omega)}\right)\) is the phase lag. Starting from a microscopic classical Hamiltonian dynamics, one can show under fairly general conditions that such a stationary LRF is related to equilibrium autocorrelation function (ACF) \(\langle \delta x(t)\delta x(0)\rangle_{\text{eq}}\) of the variable \(x(t)\) as \[24, 25, 114\]

\[
\chi(t) = -\frac{H(t) d}{k_BT dt} \langle \delta x(t)\delta x(0)\rangle_{\text{eq}} ,
\]

where \(H(t)\) is the Heaviside step function. This fundamental result in statistical physics is known as classical fluctuation-dissipation theorem (FDT) in the time domain. For the population dynamics considered, such a normalized stationary ACF should coincide with the corresponding relaxation function \(R(t)\). This statement is known as Onsager regression hypothesis. It is expected to be true in the studied semi-classical case, even if it is generally incorrect within a quantum-mechanical setting due to zero-point quantum fluctuations \[41\]. In the case of Mittag-Leffler relaxation, the LRF reads \[42\]

\[
\hat{\chi}(\omega) = \frac{\chi_0}{1 + (-i\omega\tau_r)^{\alpha}}
\]

in the frequency domain, with static \(\chi_0 = 1/\kappa\). It corresponds to the Cole-Cole response \[43\]. The one of the Davidson-Cole response is \[63\]

\[
\hat{\chi}(\omega) = \frac{\chi_0}{(1 - i\omega\tau_r)^{\alpha}}.
\]

The normalized stationary autocorrelation function of electron fluctuations between two sites of localization must also coincide with the corresponding relaxation function \(R(t)\). Therefore, the linear response of electronic degrees of freedom is also expected to be of the Cole-Cole type, but with a different time constant \(\tau_{ad}\) instead of \(\tau_r\), which might misleadingly allude to some quantum-mechanical effects in view of a power law dependence on temperature. Formally, this statement is valid, of course, only when the both asymptotics, \[27\] and \[28\], coincide. However, the asymptotics \[27\] is more relevant for the population relaxation, and therefore one can expect that such a Cole-Cole response will be approximately valid generally, for not too large frequencies. It must be also stressed the same relaxation function obtained within a CTRW related theory of FFPE with divergent mean residence times in traps does not correspond to the Cole-Cole response, contrary to a common and very influential misapprehension in the current literature \[44\]. This is because the corresponding stationary ACF within such a CTRW theory is just a constant \[94\] and, therefore, the linear response to periodic perturbances is absent asymptotically (“death of stationary response”). A common fallacy has been originated by identifying the zero-age ACF, obtained within the related CTRW theory, with the stationary one. Unfortunately, it still dominates CTRW theories of anomalous response, even if it has already been explained and remedied.
3. Nonadiabatic ET

Next, it is important to notice that the inversion of $R(s)$ to the time domain can be done exactly for $\alpha = 0.5$, for any $V_{\text{un}}$, within the approximation [27] taken for granted uniformly. Namely such a case, will be treated numerically below. This inversion reads,

$$R(t) = \frac{1}{2} \left( 1 + \frac{k_{\text{ad}}}{\sqrt{R_{\text{ad}}^2 - 4k_{\text{ad}}}} \right) E_{1/2}(-\zeta_1 \sqrt{t/\tau_{\text{ad}}})$$

$$+ \frac{1}{2} \left( 1 - \frac{k_{\text{ad}}}{\sqrt{R_{\text{ad}}^2 - 4k_{\text{ad}}}} \right) E_{1/2}(-\zeta_2 \sqrt{t/\tau_{\text{ad}}})$$

where $E_{1/2}(-z) = e^z \text{erfc}(z)$ is Mittag-Leffler function of index 1/2 expressed via the complimentary error function. Furthermore, $k_{\text{ad}} = k_{\text{na}} \tau_{\text{ad}}$ is an adiabaticity parameter, and $\zeta_1 = k_{\text{ad}} (1 + \sqrt{1 - 4/k_{\text{ad}}})/2$. Here, $k_{\text{na}} = k_{1}^{(\text{na})} + k_{2}^{(\text{na})}$ is the total nonadiabatic rate. This is an important result to be checked against numerics because of its simplicity and the insights it provides. In the adiabatic transfer regime, $\kappa_{\text{ad}} \gg 1$, $\zeta_1 \approx 1$ and $\zeta_2 \approx \kappa_{\text{ad}}$. In this case, $R(t) \approx E_{1/2}(-\sqrt{t/\tau_{\text{ad}}})$. For $\kappa_{\text{ad}} < 4$, $\zeta_1$ and $\zeta_2$ are complex-conjugated with the real part 1/2.

Furthermore, the asymptotic behavior of $R(t)$ is universal, as follows from [27]:

$$R(t) \sim \frac{1}{\Gamma(1-\alpha)} \left( \frac{\tau_{\text{ad}}}{t} \right)^{\alpha}, \quad t \to \infty$$

This behavior in Eq. [42] has not been found earlier for ET in non-Debye environments. In fact, the algebraic scaling of tail with time, $R \propto 1/t^{\alpha}$, apart from a nontrivial time constant $\tau_{\text{ad}}$ entering it, reflects the behavior of the autocorrelation function of fractional Gaussian noise $\xi_n(t)$. It worth noting that a similar heavy tail was found also in the relaxation of a two-level quantum-mechanical system driven by a very different two-state stationary non-Markovian noise whose autocorrelation function exhibits, however, the same power law scaling in its asymptotic decay [114]. Hence, it seems to be a generic feature, independently of the noise amplitude statistics, being primarily determined by the scaling of its ACF. Given this result, it seems first questionable that non-adiabatic ET transfer regime of Debye solvents, with

$$R(t) = \exp[-k_{\text{na}}t],$$

the residual power-law tail starts at some transition time $t_c$, which can be found from an approximate matching condition

$$\exp[-k_{\text{na}}t_c] = \frac{1}{\Gamma(1-\alpha)} \left( \frac{\tau_{\text{ad}}}{t_c} \right)^{\alpha},$$

solved for a large $t_c/\tau_{\text{ad}}$. The corresponding real solution reads

$$t_c = -\tau_{\text{ad}} \frac{\alpha}{\kappa_{\text{ad}}} \text{LambertW} \left(-1, -\frac{\kappa_{\text{ad}}}{\alpha (1-\alpha)^{1/\alpha}} \right)$$

where LambertW$(-1, x)$ is a $-1$ branch of the Lambert special function [115]. In the nonadiabatic anomalous ET regime, the adiabaticity parameter $\kappa_{\text{ad}} \ll 1$. For example, for $\alpha = 0.5$ and $\kappa_{\text{ad}} = 0.01$, $t_c \approx 350.155 \tau_{\text{ad}}$, and the corresponding $R(t_c) \approx 0.0301$, i.e. about 97% of population relaxation is nearly exponential and well described by the non-adiabatic MLD rate. However, the rest 3% follows an algebraically slow approach to equilibrium. Another example, for $\kappa_{\text{ad}} = 0.001, t_c \approx 4811.776 \tau_{\text{ad}},$ and $R(t_c) \approx 0.0081$. Clearly, in a deeply nonadiabatic ET regime a heavy tail with such a small initial amplitude can be masked by the population fluctuations, see below, be buried in them, and, hence, not detectable. Therefore, beyond any doubts a non-adiabatic ET does exist in the sense described even in dynamically anomalously slow environments.

B. Survival probabilities in electronic states: an equilibrium ensemble perspective

Let us now pose the question: What is the survival probability $F_i(t)$ of electron in the state $i$ before it switches to another state for the first time? To answer this question one should forbid the return of electron after it made the transition, i.e. to put to zero either $k_1(t) \rightarrow 0$ or $k_2(t) \rightarrow 0$ in Eq. [20], and either $k_{1}^{(\text{na})} \rightarrow 0$, or $k_{2}^{(\text{na})} \rightarrow 0$ in the denominator of Eq. [20]. Then, the answer follows immediately in the Laplace-space from Eq. [20]:

$$F_i^{(\text{ens})}(s) = \frac{1 + \tilde{\tau}_i(s)k_i^{(\text{na})}}{s[1 + \tilde{\tau}_i(s)k_i^{(\text{na})}] + k_i^{(\text{na})}}.$$  

For the model under study, the long-time behavior of $F_i^{(\text{ens})}(t)$ displays the same universal feature,

$$F_i^{(\text{ens})}(t) \sim \frac{1}{\Gamma(1-\alpha)} \left( \frac{\tau_{\text{ad}}}{t} \right)^{\alpha}, \quad t \to \infty$$

but with a different constant $\tau_{\text{ad}} = \tau_r \left( E_i^{(a)}/k_B T \right)^{1/\alpha}$. Likewise, all the above discussed features of $R(t)$ apply to $F_i^{(\text{ens})}(t)$ upon putting $\tau_{\text{ad}} \rightarrow 0$, or $\tau_{\text{ad}} \rightarrow 0$, respectively, in the corresponding expressions for $R(t)$. The most striking feature of the corresponding RTD, $\psi(t) = -dF_i(t)/dt \propto 1/t^{1+\alpha}$ is that it does not have a finite mean. For the case of $\alpha = 0.5$ and for the
parameters where the approximation (27) works uniformly, the corresponding \( F^{(na)}_i(t) \) are given by the rhs of Eq. (41), with \( \tau_{i,ad} \) instead of \( \tau_{ad} \), and \( \kappa_{i,ad} \) replaced by \( \kappa_{i,ad} = k^{(na)}_i \tau_{ad} \). Accordingly, \( \zeta_{i,2} = \kappa_{i,ad} (1 \pm \sqrt{1 - 4/\kappa_{i,ad}}) / 2 \), instead of \( \zeta_{1,2} \).

C. Statistics of single-electron transitions

The result in Eq. (46) does not describe, however, the statistics of single-electron transitions, \( F^{(sgl)}_i(t) \). Indeed, each jump of electron occurs at one and the same (in the contact approximation) very non-equilibrium value \( x^* \) of the reaction coordinate. This is very different from the assumption about a thermally equilibrated reaction coordinate resulting in Eq. (46). As a matter of fact, the quantum nature of electron transitions is indispensable even in the classical adiabatic ET regime, when it is considered on the level of single trajectories. This leads to a quantum breaking of ergodicity even in Deby solvents. To derive the statistics of single-electron transitions from generalized Zusman equations one must think differently [12, 13, 40]. Indeed, let an electron to start in the state \( i \) at time \( t_0 = 0 \) with the reaction coordinate fixed at \( x' \). Then, at time \( t \), \( p_i(x, t) \) obeys an integral equation [117]

\[
p_i(x, t) = G_i(x, t|x') - \int_{t_0}^{t} dt' G_i(x, t - t'|x') K(x') p_i(x', t').
\]

(48)

We are interested in the survival probability in this state and therefore consider only sink \( K(x) \) out of this state. With \( K(x) = v_0 \delta(x - x^*) \) this yields

\[
p_i(x, t) = G_i(x, t|x') - v_0 \int_{t_0}^{t} dt' G_i(x, t - t'|x^*) p(x^*, t').
\]

(49)

The Laplace-transform of this equation gives

\[
\tilde{p}_i(x, s) = \tilde{G}_i(x, s|x') - v_0 \tilde{G}_i(x, s|x^*) \tilde{p}(x^*, s),
\]

(50)

and from it one can find \( \tilde{p}_i(x, s) \),

\[
\tilde{p}(x^*, s) = \frac{\tilde{G}_i(x^*, s|x')} {1 + v_0 \tilde{G}_i(x^*, s|x^*)}. 
\]

(51)

The survival probability in the state \( i \) is \( F_i(t) = \int_{-\infty}^{\infty} p_i(x, t)dx \), and hence from Eqs. (50), (51), and using normalization of Green function, \( \int G_i(x, t|x')dx = 1 \),

\[
\tilde{F}_i(s) = \frac{1}{s} [1 - v_0 \tilde{p}_i(x^*, s)] = \frac{1 + v_0 \tilde{G}_i(x^*, s|x^*) - \tilde{G}_i(x^*, s|x')} {s + v_0 s \tilde{G}_i(x^*, s|x^*)}. 
\]

(52)

Now, if the initial \( x' \) is taken from the equilibrium distribution of the reaction coordinate, then one must replace \( G(x, t|x') \) with \( p_i^{(eq)}(x) \) in the first line of Eqs. (48), (49) and also \( \tilde{G}_i(x^*, s|x') \) with \( p_i^{(eq)}(x^*)/s \) in Eq. (52). Then, upon taking Eq. (24) into account and the fact that \( k_i^{(na)} = v_0 p_i^{(eq)}(x^*) \) we immediately reproduce the result in Eq. (40). This is just another way to derive it. However, for the statistics of single trajectories one must take \( G_i(x^*, s|x^*) = G(x, t|x') \) in Eq. (52), which yields

\[
\tilde{F}_i^{(sgl)}(s) = \frac{1}{s[1 + \tilde{\tau}(s)k^{(na)}_i] + k^{(na)}_i} 
\]

(53)

instead of (46). The difference is, in fact, huge. First of all, with Eq. (27) in (53), one can see immediately that the mean residence time in the electronic states \( \langle \tau_i \rangle = \lim_{\tau \rightarrow 0} F_i^{(sgl)}(s) \), not only exists, but it equals always the inverse MLD rate, \( \langle \tau_i \rangle = 1/k^{(na)}_i \). This is a very important result. It shows how misleading can an equilibrium ensemble theory perspective be for the single-trajectory statistics! The result in Eq. (53) is equivalent to one in Eq. (2) of Ref. [40] by Tang and Marcus for the RTD \( \tilde{\psi}_i(s) \) therein (our notations are different), which can be obtained as \( \tilde{\psi}_i(s) = 1 - s \tilde{F}_i^{(sgl)}(s) = \tilde{\hat{p}}_i(x^*, s) \).

However, our form is better because it allows to escape some pitfalls in the analysis possible especially in the case of finite adiabatic times \( \tilde{\tau}_{1,2}(0) \). It predicts a very different from the equilibrium ensemble perspective power-law for the electron RTDs, \( \psi_i(t) \propto 1/t^{2+\alpha} \), for large sojourn time intervals. Indeed, with (27) in (53) one can show upon using some identical transformations and a Tauberian theorem [118] that

\[
F_i^{(sgl)}(t) \sim \frac{1}{k^{(na)}_i \tau_r} \frac{2\alpha E_i^{(a)}}{(1 - \alpha) k_B T} \left( \frac{\tau_r}{t} \right)^{1+\alpha},
\]

(54)

for \( t \gg \tau_r \), and \( \psi_i(t) \) is a negative derivative of this result. Notice that (54) is very different from (47).

However, we will show soon that this prediction is wrong: For the considered non-Markovian dynamics, the tail of distribution is very different. It is a stretched exponential, and the generalized Zusman equations fail to describe it. The situation here is very different from the Markovian dynamics, where Eq. (53) was very successful to predict the statistics of single trajectories [13]. In the present case, quantum breaking of ergodicity combines with the classical one, caused by an algebraically slow dynamics of the reaction coordinate. This leads to a new dimension of complexity.

In an important particular case of \( \alpha = 0.5 \) and for (27)
used for all $s$,

$$F_i^{(sgl)}(t) = \frac{1}{2} \left( 1 + \frac{\kappa_{i,ad}}{\sqrt{\kappa_{i,ad}^2 - 4\kappa_{i,ad}}} \right) \times E_{1/2} \left( -\zeta^{(i)}_2 \sqrt{t/\tau_{i,ad}} \right) + \frac{1}{2} \left( 1 - \frac{\kappa_{i,ad}}{\sqrt{\kappa_{i,ad}^2 - 4\kappa_{i,ad}}} \right) \times E_{1/2} \left( -\zeta^{(i)}_1 \sqrt{t/\tau_{i,ad}} \right).$$

(55)

The formal difference with the corresponding expression for $F_i^{(ens)}(t)$ seems really small and subtle. However, the consequences are really profound! Indeed, in the adiabatic regime the main behavior of $F_i^{(sgl)}(t)$ covering about 70-90\% of survival probability initially is given by $F_i^{(sgl)}(t) \approx E_{1/2} \left(-\sqrt{t/\tau_{i,sgl}}\right)$, where

$$\tau_{i,sgl} \approx \tau_{i,ad}/\kappa_{i,ad}^2 = 1/[(k_{i}^{(na)})^2]\tau_{i,ad}. \quad (56)$$

For example, for $\kappa_{i,ad} = 10$, $\tau_{i,sgl}$ is 100 times (!) smaller than $\tau_{i,ad}$ entering formally the same approximate (for the initial times) expression for $F_i^{(ens)}(t)$ with the only difference: $\tau_{i,ad}$ instead of $\tau_{i,sgl}$. Furthermore, to be more general and to go beyond a very restrictive case of coinciding (27) and (28), we should use a different from $\tau_{i,ad} = 4\pi T_{1,2}^2$ expression for $\tau_{i,ad}$. Namely, one should use the one stemming from the short-time/large-$s$ asymptotics in Eq. (28) that yields $\tau_{i,ad} \approx (\pi/2)\tau_{0}e^{2r_{1,2}}$, for $r_{1,2} \gg 1$. With this in Eq. (56) we obtain

$$\tau_{i,sgl} \approx \frac{2\hbar^2\lambda k_B T}{\pi^2 V_{\text{tin}}^{-1/2}} \quad (57)$$

Notice, that the Debye relaxation time $\tau_{0}$ enters this expression, and not $\tau_{r}$. Eq. (57) coincides with one by Tang and Marcus in Ref. [12] and slightly differs from one in [13]. In the case of divergent $\tau_{r,2}(0)$, the result in Eq. (57) seems preferable. The major statistics of single-electron transitions in the present model in the adiabatic limit is defined by a short-ranged normal diffusion in the vicinity of the crossing point with a modification caused by anomalous diffusion. It must be emphasized again that the statistics of electron transitions viewed from the equilibrium ensemble perspective of $F_i^{(ens)}(t)$ is very different. It is primarily determined by anomalous diffusion. The difference is huge! Furthermore, the exact asymptotics for large $t \gg \tau_{r}$ is given by Eq. (57) with $\alpha = 0.5$, both in adiabatic and nonadiabatic regimes.

1. Short-and-intermediate time statistics in the strictly sub-Ohmic case

Let us consider also a strictly sub-Ohmic case with $\eta_0 = 0$. Unfortunately, in this case there is no simple analytical results available on the whole time scale. However, one can derive a short time asymptotics from Eqs. (53), (20), using the limit $s \to \infty$ and an Abelian theorem. In doing so, we obtain

$$F_i^{(sgl)}(t) \approx E_{1-\alpha/2} \left[-\left(\frac{t}{\tau_{i,sgl}}\right)^{1-\alpha/2}\right], \quad (58)$$

with

$$\tau_{i,sgl} \approx \tau_r \left(\frac{\hbar \sqrt{\lambda k_B T}}{\sqrt{\pi} T (1+\alpha)/2 (1-\alpha/2) \tau_r V_{\text{tin}}^{2/\alpha}}\right)^{2/\alpha}. \quad (59)$$

for $\exp(-r_i) \ll 1$, i.e. for a sufficiently large activation energy. This is a very nontrivial result. For $t \ll \tau_{i,sgl}$, it predicts that

$$F_i^{(sgl)}(t) \approx \exp\left[-(\Gamma t)^{1-\alpha/2}\right], \quad (60)$$

is stretched exponential with a rate parameter

$$\Gamma \approx \frac{1}{\tau_r} \left(\frac{\sqrt{\pi} T (1+\alpha)/2 \tau_r V_{\text{tin}}^{2/\alpha}}{\hbar (1-\alpha/2) \sqrt{\lambda k_B T}}\right)^{2/\alpha}. \quad (61)$$

This result yields RTDs $\psi_i(t) \propto (1-\alpha/2) \exp\left[-(\Gamma t)^{1-\alpha/2}\right]/(\Gamma t)^{\alpha/2}$, which for $\Gamma t \ll 1$ agrees with the result by Tang and Marcus in Ref. [40]. Furthermore, Eq. (60) predicts $F_i^{(sgl)}(t) \propto 1/(\Gamma t)^{1-\alpha/2}$ for intermediate times $\tau_{i,sgl} \ll t \ll \tau_r$, which agrees with the corresponding $\psi_i(t) \propto 1/(\Gamma t)^{2-\alpha/2}$ obtained by Tang and Marcus for a Davidson-Cole medium. This prediction is, however, wrong, see below, because of a principal failure of non-Markovian Zusman equations. Finally, the same asymptotics (57) describes the long time behavior. This theoretical result is, however, also disproved by numerics based on single trajectories. These two failures signify a principal failure of non-Markovian Zusman equations to describe statistics of single-electron events.

IV. SINGLE TRAJECTORY PERSPECTIVE AND STOCHASTIC SIMULATIONS

Now we wish to compare the ensemble perspective based on the generalized Zusman equations with precise simulations based on a single-trajectory perspective. For this, we perform a Markovian embedding of GLE dynamics (5) following a well-established procedure [14, 15]. It allows to get numerical results with a well-controlled numerical accuracy. To this end, the power-law memory kernel, which corresponds to the Caputo fractional derivative, is first approximated by a sum of exponentials,

$$\eta(t) = \sum_{i=1}^{N} k_i \exp(-\nu_i t), \quad (62)$$
with the relaxation rates \( \nu_i \) and elastic constants \( k_i \) obeying a fractal scaling \[14, 12, 11\], \( \nu_i = \nu_0/b^i \), \( k_i = C_\alpha(b)\nu_0^\alpha/\Gamma(1-\alpha) \propto \nu_0^\alpha \). Here, \( C_\alpha(b) \) is some constant, which depends on \( \alpha \) and is a scaling parameter \( b \). This approximation works well between two memory cutoffs, a short-time cutoff \( \tau_1 = b/\nu_0 \) and a large-time cutoff \( \tau_\theta = b^{N-1}/\nu_0 \). Already for the decade scaling with \( b = 10 \), one arrives at the accuracy of 4% for \( \alpha = 0.5 \), with \( C_{0.5}(10) \approx 1.3 \). Moreover, with \( b = 2 \) and \( C_{0.5}(2) \approx 0.39105 \) it can be improved up to 0.01% \[120\], if necessary. Next, one introduces a set of auxiliary overdamped Brownian quasi-particles with the coordinates \( y_j \). They are elastically coupled to the reaction coordinate with coupling constants \( k_j \) and are subjected to the viscous friction with the friction coefficients \( \eta_j = k_j/\nu_j \) and the corresponding thermal noises related to the friction by the FDT. For the dynamics in the quantum state \( i \) we have:

\[
\eta_0 \dot{x} = -\kappa(x - x_0\delta_{i,2}) - \sum_{j=1}^{N} k_j (x - y_j) + \xi_0(t),
\]

\[
\eta_j \dot{y}_j = k_j (y_j - y_j) + \xi_j(t),
\]

(63)

where \( \xi_j(t) \) are \( N \) additional uncorrelated white Gaussian noises, \( \langle \xi_j(t)\xi_j(t') \rangle = 2k_B T \eta_j \delta_j \delta(t - t') \). Notice, that for the model with \( \eta_0 = 0 \), the first equation in (63) yields \( x = (\sum_{j=1}^{N} k_j y_j + \kappa x_0 \delta_{i,2})/(\kappa + \sum_{j=1}^{N} k_j) \), at all times, which is used together with the second equation in (63) to formulate the corresponding stochastic algorithm. In this work, we numerically deal, however, primarily with the case of \( \eta_0 \neq 0 \).

The dimension \( N + 1 \) of a Markovian embedding of non-Markovian one-dimensional dynamics is chosen sufficiently large, so that \( \tau_0 \) exceeds the largest characteristic time of the simulated dynamics, e.g. the largest residence time in a state occurring in the simulations. It should be noticed that the Prony series expansions \[12\] of power law memory kernels similar to one we use naturally emerge within a polymeric dynamics \[12\], however, with a different rule in the hierarchy of relaxation rates \( \nu_i \). Namely, \( \nu_i = \nu_0^i p \) with \( k_i = \text{const} \) rather than \( \nu_i = \nu_0^i/b^i \), in terms of some lowest relaxation rate \( \nu_1 = 1/\tau_0 \), which yields \( \eta(t) \propto 1/t^{1/p} \) between two cutoffs \[120\]. For example, the Rouse polymer model corresponds to \( p = 2 \) with \( \alpha = 0.5 \) \[122\]. The corresponding Markovian embedding, which would reproduce the results of this paper, would be extraordinary large, about \( 10^5 \) \[31\]. Clearly, it would be simply not feasible numerically. Nevertheless, this existing relation to polymeric model provides a very good justification of our numerical approach. It is especially well suitable to model anomalous dynamics of the reaction coordinate in proteins. The choice of a particular Markovian embedding is a trade-off between the numerical accuracy and feasibility of simulations, which can run for an extraordinary long time. [Some simulations run for a month on a standard PC]. This is the reason why we choose an embedding with \( b = 10 \), rather than \( b = 2 \). With \( N = 12 \), and \( \nu_0 = 10^3 \) for \( \alpha = 0.5 \) and \( \eta_0 = 0.1 \), this choice allows to arrive at the numerical accuracy of about 5% in stochastic simulations.

The time in simulations is scaled in the units of Cole-Cole relaxation time \( \tau_r \), and the scaled \( \eta_0 \) corresponds to the initial Debye relaxation time \( \tau_0 \) in the units of \( \tau_r \). The corresponding initial stage of the reaction coordinate relaxation is almost not seen on the relevant scale of initial stretched exponential relaxation \( \tau_r \), see in Ref. \[70\]. However, it plays a crucial role in the single-trajectory statistics, being one of profound manifestations of quantum breaking of ergodicity in electron transfer. Furthermore, reorganization energy \( \lambda \) is scaled in the units of \( \hbar/\tau_{sc} \). For example, for \( \tau_{sc} = 2 \) ps (about Debye relaxation time in the bulk water), \( \tau_{sc} \) is about 2.5 cm\(^{-1} \) in spectroscopic units. Scaled temperature \( k_BT \) will be fixed to 0.1 of scaled \( \lambda/\tau_{sc} \). For example, a room temperature corresponds to \( \lambda \approx 2000 \text{ cm}^{-1} \approx 0.25 \text{ eV} \). Such values of \( \lambda \) are typical for ET in proteins, or related molecular structures, e.g. for azurin dimer \[127\]. The tunnel coupling is scaled in the units of \( \lambda/\tau_{sc} \). For example, for a typical \( \tau_{sc} = 2 \mu \text{ s} \) (about Debye relaxation time in the bulk water), \( \tau_{sc} \) is scaled in 10\(^{-3} \lambda \). Given the results of this work, adiabatic ET regime can occur in a Cole-Cole medium for rather small tunnel couplings. It should be a great surprise for many ET researchers. For example, in azurin dimer, \( \tau_{sc} = 2.5 \times 10^{-6} \text{ eV} \) \[127\]. If to assume \( \tau_r = 2 \mu \text{ s} \), it would correspond to \( \tau_{sc} = 0.01 \) in our scaled units. However, for \( \tau_r = 10 \text{ ns} \), it would be already \( \tau_{sc} = 10^{-4} \). Whereas the latter one would clearly correspond to non-adiabatic ET even in a Cole-Cole environment, see below, the former one would result into an anomalous adiabatic ET, contrary to intuition, which misleads for such a tiny value of \( \tau_{sc} \).

Simulations of Eq. (63) are done using stochastic Heun algorithm with a time step of integration \( \delta t \) which varied from \( \delta t = 10^{-4} \) (maximal) to \( \delta t = 10^{-7} \) (minimal) to arrive at reliable results. If the crossing point \( x^* \) is met between two subsequent positions of the reaction coordinate, \( x_{k+1} \), \( x_k \), a corresponding instant velocity is calculated as \( v_k = (x_{k+1} - x_k)/\delta t \), and then one decides if a jump occurs onto the different electronic curve, or not, in accordance with the probability in Eq. \[1\]. Notice that even if formally \( v_T^2 \approx \infty \) within the overdamped model, \( v_T \) in numerics is always finite. However, a linearization of Eq. \[1\], in fact, naturally occurs. Eq. \[1\] was used for generality, to avoid an additional approximation. In numerics, we considered the symmetric case of \( c_0 = 0 \), with activation barriers \( r_1 = r_2 = r = \lambda/(4k_BT) = 2.5 \).}

V. RESULTS AND DISCUSSION

A. Population dynamics

First, we studied numerically the dynamics of populations. For this, \( M = 10^4 \) particles were propagated, all
started in one electronic state, with the reaction coordinate initially equilibrated, and each making huge many transitions between two electronic states during the relaxation process. The result for the relaxation function $R(t)$ is shown in Fig. 1 for five different values of scaled $V_{\text{tun}}$. Two cases correspond to anomalous adiabatic ET, as explained in the Fig. 1 caption. Two others correspond to anomalous non-adiabatic regime, and one to an intermediate case close to the adiabatic regime. Notice a remarkable agreement between the theory based on the generalized Zusman equations, namely the result in Eq. (41), and the trajectory simulations both in the adiabatic regime and nonadiabatic regime. Deep adiabatic regime starts already from $V_{\text{tun}}=0.04$ in Fig. 1 which corresponds e.g. to $V_{\text{tun}}=1 \times 10^{-5}$ eV for $\tau_r=2$ $\mu$s and $\tau_{sc}=2$ ps, in physical units. Even for $\tau_r=50$ ps (a typical value for fractional protein dynamics, which can be attributed to fractons), the corresponding value $V_{\text{tun}}=2 \times 10^{-3}$ eV is pretty small. Such small values of $V_{\text{tun}}$ indicate that the medium dynamics can enslave ET, in the ensemble sense, and make it adiabatic even for very small tunnel couplings. In such a deeply adiabatic regime, anomalous ET is well described by a simple dependence $R(t) \approx E_{1/2}^{-1} \gamma t \exp\left\{-\frac{\sqrt{\tau_{ad}}}{\tau_{ad}}\right\} = \frac{e^{\gamma/\tau_{ad}}}{\sqrt{\tau_{ad}}}$. Notice that one cannot define here a proper adiabatic rate, and the quantity $\gamma_{1/2} = 1/\sqrt{\tau_{ad}}$ can be interpreted as a fractional adiabatic ET rate of the fractional order 1/2. Initially, for $t \ll \tau_{ad} = 4\pi [E^{(s)}/k_B T]^2 = \tau_r \lambda^2/(2k_B T)^2$, $R(t) \approx \exp\left[-2t/\tau_{ad}\right]$ is stretched exponential. For $t \gg \tau_{ad}$, a power law tail emerges, $R(t) \sim (\lambda/2k_B T)/\sqrt{\pi t}$. The agreement with the theory implies that the result in Eq. (12) is universally valid also for other values of $\alpha$, and $\gamma_0$, including $\gamma_0=0$. Also in the non-adiabatic ET regime this universal behavior is seen in Fig. 1 even if it becomes buried in the population fluctuations due to a finite $M$ (mesoscopic noise) with diminishing $V_{\text{tun}}$. Indeed, for $R(t) \sim 1/\sqrt{\pi t}$ and below, which is 0.01 or 1% for $M=10^4$ in Fig. 1, the relaxation becomes masked by the population fluctuations. Likewise, this feature may be blurred by noise also in real experiments. It is expected to be a universal feature of sub-Ohmic incoherent dynamics. The analytical result in Eq. (28) predicts for $V_{\text{tun}}=5 \times 10^{-4}$ in Fig. 1 that the crossover time $t_c$ to the power law behavior is $t_c \approx 2.146 \times 10^4$, and the corresponding $R(t_c) \approx 0.0193$, i.e. nearly 2% of the rest population relaxation follows a universal power law. This agrees with numerics fairly good in Fig. 1. However, a good agreement with the theoretical values of $t_c$ and $R(t_c)$ is not expected for larger tunnel couplings because then the major kinetics deviates strongly from a single-exponential. It is rather stretched exponential, see in Fig. 1 for $V_{\text{tun}}=1 \times 10^{-3}$. One can regard the power exponent $\gamma$ of stretched-exponential larger than 0.95 as one close to $\gamma=1$ of single exponential. Then, Eq. (15) is expected to work. The value $\gamma \approx 0.925$ for $V_{\text{tun}}=1 \times 10^{-3}$ is not that close. The importance of the analytical result in Eq. (15) lies in the fact that it allows to correctly predict $t_c$ and the weight $R(t_c)$ of the power law relaxation tail for such small $V_{\text{tun}}$, which are not attainable for a numerical analysis. For example, to obtain the relaxation curve for $V_{\text{tun}}=5 \times 10^{-4}$ in Fig. 1 it took more than one month of the computational time on a standard modern PC. The numerics are hardly feasible on standard PCs already for $V_{\text{tun}}=1 \times 10^{-3}$, with the same numerical accuracy.

B. Electronic transitions from the equilibrium ensemble perspective

The next important question we address is: What is the survival probability of electrons in an electronic state from the equilibrium ensemble perspective? To answer...
this equation, we prepare all the electrons in one state at the equilibrated reaction coordinate (a different value is taken randomly from the Boltzmann distribution for each electron in the ensemble), and take out an electron from the ensemble once it jumps into another state at the crossing point. The numerical results are depicted in Fig. 2 in comparison with the theory results based on the generalized Zusman equations. The theory fails in a very spectacular fashion. First, the mean residence time in the state is finite, at odds with the theory predicting infinite MRT. Also the variance of RTD is finite, with a further diminishing $V_{\text{tun}}$. And nevertheless the theory predicts a very wrong power law tail, which is disproved by numerics. This failure becomes ever more visible with the increase of $V_{\text{tun}}$.

In strictly non-adiabatic limit, ET is clearly ergodic. It is well described by the MLD rate. However, some deviations from a single-exponential transfer kinetics and ergodicity become visible even for the smallest tunnel coupling in this paper. This is very different from the Markovian Debye case. One should emphasize this striking feature once more: Even if sub-Ohmic ET is strictly exponential and ergodic in the strict non-adiabatic limit from the point of view of the survival probabilities in the electronic states, the relaxation of electronic populations follows asymptotically a power law, as described above. It can, however, be very difficult to detect due to a pure statistics in real experiments. For $V_{\text{tun}} = 5 \times 10^{-4}$, the averaged numerical MRT in an electronic state is $\langle \tau \rangle_{\text{emp}} = (\langle \tau_1 \rangle + \langle \tau_2 \rangle)/2 \approx 1.0845 \times 10^4$. It nicely agrees with the theoretical prediction $\langle \tau \rangle = 1/k_1^{(na)} \approx 1.0868 \times 10^4$. The theoretical prediction of a power-law tail $F_i^{(sgl)}(t) \sim t^{-3/2}$ is, however, once again, completely wrong.

Next, for $V_{\text{tun}} = 1 \times 10^{-3}$ in Fig. 3 b, the survival probabilities in two states are somewhat different. It is unclear why statistics is visible poorer in this particular case, what caused that discrepancy. In fact, the results presented in part (a) are based on $2 \times 7583$ electronic transitions, while in part (b) on $2 \times 20603$ such transitions. A further increase in the number of transitions would definitely smear out the discrepancy in the part (b). However, it would require a much longer computational time. Nevertheless, the averaged $\langle \tau \rangle_{\text{emp}} = (\langle \tau_1 \rangle + \langle \tau_2 \rangle)/2 \approx 2.7395 \times 10^3$ agrees nicely with the theoretical $\langle \tau \rangle = 1/k_1^{(na)} \approx 2.7169 \times 10^3$. As expected, the power of stretched exponential is smaller, with the mean value $b \approx 0.935$, and discrepancy with the theory result (especially, with respect to the tail of distribution) becomes stronger. Nevertheless, the theoretical result describes very well about 98% of the survival probability decay in the state 2. With a transition to adiabatic regime, the agreement between the theory and numerics becomes worser, see in the part (c) of Ref. 13. The results for are shown in Fig. 3.
described by a stretched exponential, which tends to a single exponential with the rate given by the MLD rate $V$.

Perspectives of $\eta$ and $\eta^*$ difference. Thus, a finite but small value of $\eta$ only weakly influences survival probabilities from the equilibrium ensemble $V=0$, whereas in (f) also a strictly sub-Ohmic case $V=0.1$, is completely wrong. Survival probability is well (a) in the panel (e). This comparison does not reveal a statistically significant difference. Therefore, a finite but small value of $\eta$ only weakly influences survival probabilities from the equilibrium ensemble perspective.

FIG. 2. (Color online) Time-decay of the survival probability in the first state calculated from the trajectory simulations done using a thermal equilibrium preparation of the reaction coordinate at the initial time. Time is scaled in the units of $\tau_v$. Any single trajectory is terminated once a jump into another electronic states occurs. Statistics is derived from $10^4$ trajectories. The dashed black line depicts the theory result from Eqs. (35), (31), as described in Sec. III,B. Notice, that by a sharp contrast with Fig. 1, where a related result agrees with numerics very well, for the survival probabilities it fails completely. First, not only the mean residence time is finite (the theory predicts that it is infinite), but also the variance of RTD is finite. The corresponding numerical values of mean values and dispersion coefficients are given in different panels for different values of $V_{\text{min}}$ shown therein. Second, the theoretical tail prediction, $F_i(t) \propto t^{-\Gamma}/t^{1/2}$, is completely wrong. Survival probability is well described by a stretched exponential, which tends to a single exponential with the rate given by the MLD rate $k_1^{\text{ana}}$ in the limit $V_{\text{min}} \rightarrow 0$, see the main text for more detail. In the panels (a)-(e), $\eta = 0.1$, whereas in (f) also a strictly sub-Ohmic case of $\eta = 0$ is compared with the case of $\eta = 0.1$ in the panel (e). This comparison does not reveal a statistically significant difference. Thus, a finite but small value of $\eta$ only weakly influences survival probabilities from the equilibrium ensemble perspective.
FIG. 3. (Color online) Survival probabilities in two states vs. time (in units of $\tau_c$) from a single trajectory perspective. The numerical data are shown by symbols and their various fits (with the parameters shown in the plots) by the full lines. The results of the analytical theory based on the generalized Zusman equations in the contact approximation are depicted by the dashed black lines. In the panels (a)-(e), $\eta_0 = 0.1$. In the panel (f), $\eta_0 = 0$. The values of the tunnel coupling $V_{tun}$ are shown in the corresponding panels.
However, in the adiabatic regime it improves again. Accordingly, in the parts (d) and (e) the theory describes even about 90% and 98% of the initial decay, correspondingly. This is because, in this case the normal diffusion dominates on the corresponding time scale for the studied case of $\eta_0 \neq 0$. The theoretical prediction of a power law tail is, however, anyway wrong, completely. Interestingly, the results in the part (c) are characterized by entirely different statistics viewed from the equilibrium ensemble perspective practically does not depend on this coordinate. This is probably the most deep expression of a profound breaking of ergodicity in the adiabatic ET due to quantum effects. However, it badly fails to describe (i) the survival probabilities from the ensemble perspective, (ii) the tail of the residence time distribution in the case of single trajectories, and (iii) an intermediate power law regime in the case of a strictly subdiffusive dynamics on the level of single trajectories. This naturally provokes the question: Where and why the pertinent theory fails?

To answer this penetrating question it is naturally to use the picture of a multi-dimensional Markovian embedding utilized to simulate the single trajectories in this paper. Indeed, within the Markovian embedding scheme the Eq. (49) must be replaced by

$$p_i(x, y, t) = G_i(x, y, t|x', y')$$

where $G_i(x, y, t|x', y')$ is the Green function of the corresponding multi-dimensional Markovian Fokker-Planck equation. Its explicit form is not required to understand our argumentation. The Laplace-transformed Eq. (64) reads

$$\tilde{p}_i(x, y, s) = \tilde{G}_i(x, y, s|x', y')$$

$$-v_0 \int_{-\infty}^{\infty} dy' \tilde{G}_i(x, y, s|x', y') \tilde{p}_i(x^*, y', s).$$
However, it is difficult to solve without further approximations for \( \tilde{p}(x^*, s) = \frac{1}{\mathcal{Z}} \tilde{p}(x^*, y^*, s) \) \( dy^* \). One can use e.g. the Wilemski and Fixman approximation

\[
\tilde{p}(x^*, y^*, s) \approx \tilde{p}(x^*, s) p_{st}(y^*),
\]

where \( p_{st}(y^*) \) is the stationary distribution of the auxiliary variables. In this case, upon introduction of the reduced propagator

\[
\tilde{G}_i^\text{(red)}(x, s|x^*) = \int \int \tilde{G}_i(x, y^*, s|x^*) p_{st}(y^*) dy^* dy^*,
\]

one can see that the problem is reduced to the previous one with \( \tilde{G}_i^\text{(red)}(x, s|x^*) \) treated as a non-Markovian propagator. It is indeed nothing else the non-Markovian Green function \( \tilde{G} \), with the memory kernel in \( \tilde{G} \), which corresponds to a multi-dimensional Markovian embedding description. The principal assumption here is a fast equilibration of the auxiliary variables leading to Eqs. \( 66 \) and \( 67 \). However, this assumption is, strictly speaking, completely wrong for those modes \( y_i \), which are slow on the time scale of electronic transitions. Here, we locate precisely the reason for a principal failure of the non-Markovian Zusman equations description. It is, in fact, heavily based on the Wilemski and Fixman approximation, which cannot be justified for the slow modes of the environment. This reason for failure is precisely the same as for the failure of non-Markovian Fokker-Planck equation to describe survival probabilities of classical bistable transitions \[14 \] \[15 \]. In fact, one should wonder about why such a description sometimes works, rather than about its failure, which is generally expected. Notably, the approach based on non-Markovian Fokker-Planck equation generally fails to describe statistics of single trajectories. Although, it can properly describe the most probable value of the logarithmically transformed residence times, in the case of classical bistable transitions \[14 \] \[15 \], and the mean residence time, in the present case. Moreover, in the present case it does describe properly the initial part of the residence time distribution. However, it completely fails to describe the escape kinetics with the absorbing boundary condition at the crossing point, on the ensemble level. The reason is clear: Each electron makes a transition at a fixed, non-equilibrium and quasi-frozen realization of the reaction coordinate, whereas non-Markovian Zusman equations implicitly assume that all the environmental modes \( y_i \), which are responsible for the memory effects, are instantly equilibrated. Only in this case, one can exclude the dynamics of \( y_i(t) \) and introduce a NMFPE with Green function \( \tilde{G} \). However, if the same electron makes huge many transitions in a long run, it samples different random realizations of the reaction coordinate at each transition. Then, the problem becomes essentially softened, and the description becomes well justified, on the level of population relaxation. However, it must be used anyway with a great care, when applied to single trajectories. For example, it predicts completely wrong asymptotics of the survival probabilities, and the prediction of the correct intermediate asymptotics in the case of finite \( \eta_0 \) is just due to Markovian character of the reaction coordinate dynamics on the corresponding time scale. However, once again, when huge many particles repeatedly jump between the electronic states this kind of non-Markovian description becomes completely correct for the population relaxation. Actually, most theories of electron transfer focus namely on the population relaxation, which can be, however, quite misleading for ET in slowly fluctuating environments as this work shows.

### VII. SUMMARY AND CONCLUSIONS

In this work, we elucidated the basic features of fractional electron transfer kinetics in a Cole-Cole, subdiffusive sub-Ohmic environment both from the ensemble perspective of non-Markovian Zusman equations within the contact approximation (a truly minimal semi-classical setting), and from the perspective of single trajectories, within a closely related stochastic trajectory description. Our both analytical and numerical study convincingly showed that:

(i) In a deeply nonadiabatic ET regime, for very small tunnel couplings, the ET kinetics viewed from the perspective of survival probabilities remains ergodic even in such slowly fluctuating environments. It is exponential and well described by the Marcus-Levich-Dogonadze rate. However, at odds with this remarkable fact, the relaxation of electronic populations to equilibrium has a universal power law tail whose weight diminishes with diminishing electronic coupling. The smaller the tunnel coupling, the later sets this residual anomalous behavior in. It can be buried in noise, and hence very difficult to reveal.

(ii) The ensemble theory based on the generalized Zusman equations remarkably well predicts the relaxation of electronic populations in the whole range of permitted \( V_{\text{tun}} \) variations. Our analytical result agrees very well with stochastic trajectory simulations. In the adiabatic regime, electronic relaxation is initially stretched exponential, and then changes over into a power law. For some parameters, it is described by the same Mittag-Leffler functional dependence, which describes also the relaxation of the reaction coordinate. It corresponds to the Cole-Cole dielectric response, often measured in protein systems. However, the relaxation time parameter entering this electronic relaxation (and the related Cole-Cole response) is very different from one of the reaction coordinate. Interestingly enough, it does not depend exponentially on the height of the activation barrier, what would generally be expected (an Arrhenius dependence), but in a power law manner.

(iii) With increasing tunnel coupling, a profound violation of the kinetic ergodicity is demonstrated. Survival probabilities in electronic states start to display very dif-
different, conflicting kinetics from the ensemble and single trajectory perspectives. This violation of ergodicity occurs both on the account of long-lasting memory effects in viscoelastic environment, and due to a profound quantum nature of electron transfer on the level of single particles, even in a seemingly classical, from the ensemble point of view, adiabatic regime.

(iv) The equilibrium ensemble theory based on the generalized Zusan equations turns out to be completely wrong in predicting the kinetic behavior of the ensemble of the particles making transition to another state without return, and this work explained the reason why. The corresponding theory predicts that the residence time distribution does not possess a mean time and has a power law tail, \( \psi_i(t) \propto t^{-1-\alpha} \). The both predictions are completely wrong. Not only the mean time, but also the variance are finite. The tail is stretched exponential. The reason for failure is that the slow viscoelastic modes of the medium are quasi-frozen and not equilibrated, when electron jumps out of the state at the curve-crossing point, contrary to the basic assumption, central also for the rate theory.

(v) The non-equilibrium ensemble theory applied to describe statistics of stationary, equilibrium single electron transitions correctly predicts the mean residence time even in a deeply adiabatic regime. It is given by the inverse of MLD rate, for any medium. However, its time even in a deeply adiabatic regime. It is given by (13), except for the initial times \( \tau \leq \tau_0 \). This is also a very impressive success. However, the intermediate power law, \( \psi(t) \propto t^{-2+\alpha/2} \) does not exist, in the case of \( \alpha < 1 \). It presents an artifact of the Tang-Marcus theory of quantum dots blinking in non-Debye media, is wrong.

To develop a flawless analytic theory of non-ergodic single electron transport provides a real current challenge for the theorists. This is because the theory based on the generalized Zusan equations can deeply fail in some very important, key aspects, as our study manifested. However, the developed stochastic numerical approach to the underlying curve-crossing problem can be used reliably instead, within the same parameter range of the overall model validity. It is restricted, however, to a series of approximations, primarily to the contact approximation. To go beyond it, e.g. in the spirit of our earlier work, generalized towards non-Markovian dynamics of the reaction coordinate, provides one of the interesting directions to explore in the future. The problem is, however, much more challenging and deep. Indeed, what to do in the case of a fully quantum description? The most successful current quantum theories of electron transfer are the ensemble theories based on the concept of the reduced density matrix. Our work shows, in fact, that the related ensemble approach (in a semi-classical limit) fails overall to describe the statistics of single electron transitions in an adiabatic regime in the case of non-Debye media featured e.g. by the Cole-Cole response. This inter alia is a common situation in the case of biological electron transfer. To develop a proper fully quantum theory based on the trajectory description provides a real challenge, which the readers are invited to address.

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Appendix A: Adiabatic time-functions

This Appendix deals with functions \( \tilde{\tau}_{1,2}(s) \) in Eq. (A3), which have a rather complex structure and are not easy to analyze. They can be expressed as sums of two contributions, \( \tilde{\tau}_{1,2}(s) = \tilde{\tau}^{(1)}(s) + \tilde{\tau}^{(2)}(s) \), where \( \tilde{\tau}^{(1)}(s) \) is the Laplace-transform of

\[
 f^{(1)}(t) = \frac{1}{\sqrt{1-\theta^2(t)}} - 1 \quad (A1)
\]

and \( \tilde{\tau}^{(2)}_{1,2}(s) \) is the Laplace-transform of

\[
 f^{(2)}_{1,2}(t) = \frac{1}{\sqrt{1-\theta^2(t)}} \left( e^{2\tau_{1,2} \theta(t)/[1+\theta(t)]} - 1 \right), \quad (A2)
\]

where \( \theta(t) \) is the coordinate relaxation function and \( r_{1,2} = E^{(a)}_{1,2} = (\lambda \mp \epsilon_0)^2/(4\lambda k_B T) \) are activation energies of ET in the units of \( k_B T \). We restrict our analysis to an important parameter regime of sufficiently large activation barriers \( r_{1,2} \approx 2 \). Then, the first contribution in the sum can be neglected and we concentrate on the function \( f^{(2)}(t) \), where we drop subindex for a while. We are interested in the case \( \tau = \tau_0/\tau_r \ll 1 \), where the relaxation of the reaction coordinate can be approximately described by (A3), except for the initial times \( t < \tau_r \). Notice, that the scaled \( \tilde{\eta}_0 = \eta_0/(\eta_0 \tau_r^{1-\alpha}) = z \). Next, we consider two parameter regimes: (i) \( t \ll \tilde{\eta}_0 \tau_r \), (ii) \( t \gg \tau_r \). In the first one, \( \theta(t) \approx \exp [-1/t/(z\tau_r)] \approx 1 - t/(z\tau_r) \), and we have

\[
 f^{(2)}_{1,2}(t) \approx \frac{c_1}{\sqrt{t/\tau_r}} \quad (A3)
\]
with \( c_1 = \sqrt{\frac{n_0}{2}} (e^{r_1 \cdot 2} - 1) \) universally for any \( \alpha \). By an Abelian theorem \[118\] this yields \[25\]. In the second regime, \( \theta(t) \sim (1/(1-\alpha))(t/\tau)^\alpha \ll 1 \), and we have

\[
 f_{1,2}^{(2)}(t) \approx \frac{c_2}{(t/\tau)^\alpha} \quad (A4)
\]

with \( c_2 = 2r_{1,2}/(1-\alpha) \). By a Tauberian theorem \[118\] this yields \[27\]. In the numerical studies of this paper, we consider a symmetric ET with \( \alpha = 0.5 \), \( r_1 = r_2 = 2.5 \) and \( n_0 = 0.1 \). In this particular case, \( c_1 \approx 2.50 \) and \( c_2 \approx 2.82 \). This is the reason why the approximation \[27\] works well in the whole range of the variable \( s \), see in Fig. 4 a. This is, however, a lucky case beyond which the beauty of the related analytical results in the adiabatic ET regime is lost. Generally, short and long time asymptotics in \[A3\] and \[A4\] are very different even for \( \alpha = 0.5 \), since \( c_1 \) and \( c_2 \) can differ strongly, in general. For \( \alpha = 0.5 \), one must approximately satisfy \( c_1 \approx c_2 \), or \( \sqrt{\frac{n_0}{2}} (e^{r_1 \cdot 2} - 1) \approx 2r/\sqrt{\pi} \), for the approximation \[27\] to work uniformly. This can be done only in a symmetric case.

Furthermore, for a model with \( \eta_0 = 0 \) (strictly sub-Ohmic environment), Eq. \[A3\] is replaced for \( t \ll \tau_r \) by

\[
 f_{1,2}^{(2)}(t) \approx \frac{c_3}{(t/\tau_r)^\alpha/2} \quad (A5)
\]

with \( c_3 = \sqrt{(1+\alpha)/2} (e^{r_1 \cdot 2} - 1) \). This asymptotics yields \[29\] for \( st\tau \gg 1 \). Notice that in this case, the power-law behaviors for \( t \ll \tau_r \) and \( t \gg \tau_r \) are very different, see in Fig. 4 b. The result in \[A5\] predicts a transient power law regime in RTD for \( t < \tau_r \), with a power law exponent \( -(1+\alpha/2) \). Its realization, is, however, not warranted. This is so because this power law can be expected only for time smaller and close to \( \tau_r \), whereas for times larger than \( \tau_r \), another power law, \( -(1+\alpha) \) is expected from the generalized Zusman equations. It the considered case with a small but finite \( \eta_0 \), an intermediate power low in RTDs with power law exponent \(-1.5\) is expected, in the adiabatic ET regime. This expectation is more justified, because the both power laws, before and after \( \tau_r \), have the same exponent.

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FIG. 4. (color online) The sum \( f(t) = f^{(1)}(t) + f^{(2)}(t) \) in Eqs. (A1), (A2) (full black line), and its corresponding approximations by Eq. (A3) (dashed blue line) or and Eq. (A5) (dash-dotted red line) for the case \( \alpha = 0.5, \gamma_1 = \gamma_2 = 2.5 \) and (a) \( \gamma_0 = 0.1 \) or (b) \( \gamma_0 = 0 \). Time is in units of \( \tau \).

\[ f(t) = f^{(1)}(t) + f^{(2)}(t) \]

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