Single molecule waiting time distribution functions in quantum processes

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The statistics of single molecule blinking events often reveal underlying quantum mechanisms. The golden rule rate expression for quantum transitions is shown to be the inverse of the mean waiting time. The distribution function for the waiting time is related to the density of states such that simple power-law distribution functions can be predicted based on the functional form for the density of states. Explicit formulas are derived for waiting time distribution functions in three kinetic processes: Quantum tunneling, intersystem conversion, and nonstationary electron transfer.

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I. INTRODUCTION

Technical advances in spectroscopic and microscopic methods have made it possible to detect and image molecular dynamics and reactions of single particles. Such measurements often reveal detailed molecular information not available from ensemble averaged bulk data and thus provide a better understanding of underlying mechanisms for dynamic systems ranging from the low-temperature glass to room-temperature biological systems. A particularly interesting aspect of single molecular experiments is fluorescence blinking, which directly measures the fluorescence on and off waiting time distribution. Statistical methods to extract microscopic information from single molecule measurements pose interesting challenges for theorists. For example, using a modulated two-state reaction model, the two-event echo in single molecule kinetics can be related to the underlying conformational dynamics.

A quantum process consists of one or several quantum transitions, with rate constants determined by initial and final states. Thus, the waiting time distribution is related to the distribution of rate constants, which in turn is related to the density of quantum states. The golden rule rate constant is essentially an ensemble averaged rate constant. Due to limited temporal resolution, conventional bulk experiments are designed to measure the golden rule rate constant, whereas single molecule experiments are highly effective in obtaining the waiting time distribution, especially for slow decay and long-time correlation. This paper is organized as follows: The definition for the waiting time distribution and its relationship to the golden rule rate are clarified in Sec. I. Simple algebraic laws for the density of states and for rate constants lead to the prediction of power-law decay in Sec. II. Then, the basic formulation is applied to quantum tunneling in Sec. III, intersystem conversion in Sec. IV, and nonequilibrium electron transfer in Sec. V. Concluding remarks are given in Sec. VI.

II. WAITING TIME DISTRIBUTION AND GOLDEN RULE RATE

As illustrated in Fig. 1(a), a quantum system initially in the $i$th state decays to a set of final states with the rate constant

$$k_i = \sum_j \frac{2\pi}{\hbar} \delta(E_j - E_i) |V_{ij}|^2,$$

where $E_i$ and $E_j$ are the energy levels of the initial and final states, respectively, and $V_{ij}$ is the coupling matrix. Even with a single molecule, experimental measurements are repeated over a long period of time to collect meaningful data for statistical analysis. With standard interpretation of quantum mechanics, each measurement samples a particular quantum state according to the initial distribution and detects a particular rate constant. We assume here that initial states are fully relaxed through interactions with surroundings so that there is no phase coherence between different initial states. As shown in Fig. 1(b), each initial state represents a reaction channel with a stationary flux $F_i$, so that the waiting time distribution for the process can be expressed as

$$f(t) = \sum_i e^{-tk_i} F_i \sum_j F_j,$$  

which is related to the survival probability $S(t)$ by $S(t) = 1 - \int_0^t f(\tau) d\tau$.

As explained in a recent paper, the stationary flux depends on the specific experimental condition and the kinetics of the system. In one scenario, the system is constantly pumped back to the reactant such that the stationary flux becomes $F_i = k_i \rho_i$. The waiting time distribution takes the form of

$$f(t) = \sum_i \frac{e^{-tk_i} \rho_i^2}{\sum_j k_j \rho_j},$$

where $\rho_i$ is the equilibrium population distribution of the $i$th initial state. The average waiting time is given by

$$\langle t \rangle = \int_0^\infty f(t) t dt = \frac{\rho_i}{\sum_i k_i \rho_i} = \frac{1}{k_{GR}},$$

where

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which recovers the golden rule (GR) rate expression \( k_{\text{GR}} = \sum ik_i \rho_i \). In fact, it is shown in a recent paper,\(^{19}\) the mean survival time is equivalent to the ensemble averaged golden rule rate, as long as the reactive system is stationary. In another possible scenario, single molecule experiments are repeated with the same initial preparation so that the flux is proportional to the initial population distribution. Then, we have the waiting time distribution as

\[
f(t) = \sum_i e^{-k_i t} \rho_i,
\]

and the average waiting time as

\[
\langle t \rangle = \sum_i \frac{\rho_i}{k_i} / \sum_i \rho_i,
\]

where the normalization condition \( \sum \rho_i = 1 \) is implied. The difference between Eqs. (4) and Eq. (6) lies in the definition of \( f(t) \), which is based on the occurrence of quantum transition events. In nonequilibrium thermodynamics, the rate constant is extracted from the relaxation process to the equilibrium population distribution, thus making no difference between the above two scenarios. Usually, the initial population peaks within a narrow distribution so that the difference between Eqs. (3) and Eq. (6) is not significant. For simplicity, our discussion in the rest of this paper will use Eq. (5).

The average over the initial distribution in Eq. (2) is valid only if there is no fixed phase relation between different quantum states. As implied in the derivation of the golden rule rate expression, fast dephasing is required to reduce quantum dynamics to classical kinetics. In the initial preparation by an ultrafast laser pulse or between fast quantum transitions, the phase relation is not dissipated by fluctuating environments before a transition to another state. Then, one has to calculate the waiting time distribution by taking into account the evolution of the density matrix, which will not be discussed in this paper. Careful analysis of single molecule experiments in quantum systems raises interesting questions regarding quantum measurements, coherence and dephasing, and the bath–system separation. Wolynes and co-workers\(^{20}\) have demonstrated that the interference between different paths results in quantum twinkling, i.e., the nontrivial moments of the system wave function, which cannot be fully described by the reduced description after bath averaging. Makarov and Metiu have shown how the radio frequency (rf) radiation can be used to control the statistical properties of the photon emission events of a single molecule.\(^{21}\)

### III. POWER-LAW DECAY AND DENSITY OF STATES

Equation (5) can be written in a continuous form as

\[
f(t) = \int \exp[-k(E)t] k(E) \rho(E) dE,
\]

where \( \rho(E) \) is the density of states. The integral in Eq. (7) is usually dominated by a particular range of energy, where the rate and the density of states follow the simple algebraic law: \( k(E) \propto E^r \) and \( \rho(E) \propto E^m \). As a result, Eq. (7) predicts a power law decay

\[
f(t) \propto t^{-(r+1)/r'},
\]

indicating a possible relation between the waiting time distribution function \( f(t) \) and the density of states \( \rho(E) \).

As an example, consider a quantum transition between two quasi-free particles in three-dimensional space, where \( \rho(E) \propto \sqrt{E} \). We further assume that the coupling matrix \( V_{ij} \) does not strongly depend on energy such that the rate constant is proportional to the density of final states. The energy conservation relation requires \( E_f = E_i + E_r \), where \( E_0 \) is an intrinsic energy difference or the laser carrier excitation frequency. Thus, for a given initial state, the density of final states is expanded, \( \rho(E_f) \propto \sqrt{E_0 + E_r} \), \( \sqrt{E_0 + E_r/2} \sqrt{E_0 + \cdots} \), and the corresponding rate constant is approximated as

\[
k(E_i) = k_0 + c E_i + \cdots,
\]

where \( k_0 \) is the constant part of the rate that is independent of the energy, and \( c \) is the linear coefficient. The average over initial states in Eq. (7) gives

\[
f(t) \propto \int e^{-k_0 t} e^{c E_0 t} dE \propto e^{-k_0 t},
\]

which predicts power-law decay within the time scale of \( k_0 t < 1 \). This kind of power-law dependence has been observed in single quantum dot blinking phenomena.\(^{22}\) Though the underlying mechanisms for the power law dependence in these experiments have not been fully clarified, the scaling argument presented here provides a possible interpretation.

### IV. QUANTUM TUNNELING

The quantum tunneling rate depends on the energy of the initial state in the reactant well. Under the Wentzel–Kramers–Brillouin (WKB) approximation, the tunneling rate can be expressed as

\[
k(E) \propto \exp[-S(E)/\hbar],
\]

where \( S(E) = \frac{\hbar}{\mathcal{E}} \sqrt{V(q) - E dq} \) is the semiclassical action for quantum tunneling. The corresponding waiting time probability distribution is given by
where \( \kappa^c \) contributes to the density of states, \( \tilde{S} \) noting the population deletion from the sink state.}

FIG. 2. A sketch of the intersystem conversion process, with double arrows denoting intrasystem transition rate constants, and with the thick arrow denoting the population deletion from the sink state.

\[
f(t) = \int e^{-ik(E)t} \rho(E) dE \\
\times \int e^{-ik(E)\exp[-S(E)/\hbar - \beta E]} dE / \\
\int \rho(E) dE,
\]

(12) where thermal equilibrium is assumed in the reactant well \( \rho(E) \propto e^{-\beta E} \). The stationary condition for \( \kappa(E)\rho(E) \) gives \( S'(E_0) = -\hbar \beta \), which defines the instanton rate, \( k_0 \propto e^{-S(E_0)/\hbar} \). The thickest descent evaluation of \( \kappa(E)\rho(E) \) results in

\[
\frac{S(E)}{\hbar} + \beta E = \frac{S(E_0)}{\hbar} + \frac{S''(E_0)}{2\hbar} (E - E_0)^2 + \cdots,
\]

(13) where the linear term vanishes. With the WKB approximation, Eq. (12) reduces to

\[
f(t) \propto e^{-k_0 t} \exp \left[ -\frac{(k_0 \beta t)^2 \hbar}{2S''(E_0)} \right],
\]

(14) where \( S''(E) \) is related to the van Vleck determinant for the instanton solution. The steepest descent evaluation of \( \kappa(E)\rho(E) \) results in the diagonal element of the matrix \( G \) at the crossing state. Here, the initial distribution is assumed to be in equilibrium, implying the stationary condition \( G(s)\rho_{eq} = \rho_{eq}/s \).

The Green function is expanded as \( G_c(s) = \rho_{eq}/[s + b(s)] \), with \( G_c(s) = \int_0^\infty e^{-st}[G_c(t) - \rho_{eq}] dt \), so that Eq. (17) can be rewritten as

\[
f(s) = \rho_{eq} \int \frac{k_c b(s) + 1}{k_c \rho_{eq}},
\]

(18) which can be inverted back to \( f(t) \) in real time. The average waiting time is evaluated directly from Eq. (18), giving

\[
\langle t \rangle = \frac{-\partial}{\partial s} \ln f(s) |_{s=0} = \frac{k_c b(0) + 1}{k_c \rho_{eq}},
\]

(19) where \( b(0) = \int_0^\infty [G_c(t) - \rho_{eq}] dt \). The inverse of Eq. (19), \( k = 1/t \), recovers the familiar rate expression, which has been derived in various contexts. In particular, Chernyak, Schulz, and Mukamel mapped multistate electron transfer into random walk and derived similar expressions for the waiting time distribution.

V. INTERSYSTEM CONVERSION

We consider a generic model consisting of \( N \) states with the intra-system transition rate constants given by a matrix \( K \). As illustrated in Fig. 2, the \( N \)-state system converts to another system at the \( c \) state with the rate constant \( k_c \). The kinetics of the system is described by

\[
\dot{\rho}(t) = K \rho(t) - k_c \rho_c(t),
\]

(15) where \( \rho \) is a vector corresponding to the \( N \) states \( \{\rho_i(t)\} \). The Laplace transform of the above vector equation yields

\[
\rho(s) = \frac{1}{s - K + k_c} \rho(0) = \frac{1}{1 + G(k_c)} \rho(0),
\]

(16) where \( (k_c)_ij = k_c \delta_{ij} \delta_{jc} \), \( \rho(0) \) is the initial distribution, and \( G(s) \) is the Green’s function, \( G(s) = 1/(s - K) \). The Laplace transform of the waiting time distribution function is

\[
f(s) = k_c \rho_c(s) = \frac{k_c}{1 + k_c G_c(s)} \rho_{eq}/s,
\]

VI. NONEQUILIBRIUM ELECTRON TRANSFER

The above model can be used to describe solvent-controlled electron transfer with nonequilibrium initial distribution functions. In Fig. 3, the \( N \)-state system is taken as the continuous diffusion coordinate, and the transition rate at the degenerate state \( E_c \) as \( k_c = \frac{2 \pi V^2}{\hbar} \delta(E - E_c) = \alpha \delta(E - E_c) \) with \( V \) the electronic coupling constant and \( \alpha = 2 \pi V^2/\hbar \). If the initial configuration is not equilibrated, Eq. (17) becomes

\[
f(s) = \frac{k_c}{1 + k_c G_c(s)} \rho_c(s),
\]

(20) where \( \rho_c(s) \) represents the density at the crossing state and the dot \( \cdot \) represents the integration of the diffusive reaction coordinate. Transformation to the real time leads to

\[
f(t) = \int_0^t \gamma(t - \tau) \rho_c(\tau) d\tau,
\]

(21) where \( \gamma(\tau) \) is the memory kernel defined from Eq. (20) as

\[
\gamma(s) = \frac{\alpha}{1 + \alpha G_c(s)}.
\]

(22)

FIG. 3. A sketch of the solvent-controlled electron transfer process. The nonstationary wave-packet motion is due to the nonequilibrium initial solvent distribution.
In the limit of fast decay, the Markovian approximation, 
\[ \gamma(\tau) \rightarrow \Gamma \delta(\tau), \]
can be applied to the memory kernel
\[ f(t) = \int_0^\infty \gamma(\tau) d\tau \rho_c(t) = \Gamma \rho_c(t), \]
with \( \Gamma \) the effective rate constant. The Markovian limit of \( \gamma(s_0) \) is evaluated for a time scale \( 1/s_0 \) smaller than the crossing rate \( \alpha \rho_c \), but longer than the decay time for solvent relaxation, i.e.,
\[ \left( \ln b \right)_{\tau = t_0} > s_0 > \alpha \rho_c \text{eq}, \]
so that we have
\[ \Gamma = \frac{\alpha}{1 + b(0)\alpha}, \]
where \( b(s_0) \) is approximated by \( b(0) \). For equilibrium electron transfer, \( \rho_c(t) = \rho_c \text{eq} \), the above argument leads to the solvent-controlled electron transfer rate expression.\(^{26-31}\)

In the framework of classical Marcus theory,\(^{32}\) the nonequilibrium distribution function \( \rho_c(t) \) is expressed as
\[ \rho_c(t) = \sqrt{\frac{\beta}{16\pi\lambda}} \exp\left[ \frac{-\beta}{4\lambda} \left( \lambda - E_s(t) \right)^2 \right], \]
where \( E_s(t) \) is the time-dependent solvation energy and \( \lambda \) is the reorganization energy. Applying the Debye solvation model, we have approximately the waiting time distribution for high barriers
\[ f(t) = \frac{\alpha \rho_c(t)}{1 + \alpha \tau_D / \lambda}, \]
with the solvation energy
\[ E_s(t) = E_s(0) e^{-\beta \tau_D}. \]

Similar results can also be obtained from the harmonic bath model.\(^{33-35}\) As can be seen from Eq. (26), the waiting time distribution directly measures the motion of the solvation energy in electron transfer.

**VII. CONCLUDING REMARKS**

In this paper, we have investigated single molecule waiting time distribution functions in various quantum processes, including tunneling, intersystem conversion, and nonstationary electron transfer. In addition to direct and accurate measurements of the waiting time distribution, single molecular experiments also reveal the inhomogeneities of reaction rates and possible correlations. Furthermore, the possible single molecule detection of quantum coherence and interference remains an intriguing question. These and other problems will be explored in the future.

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