Quantum dynamics with non-Markovian fluctuating parameters

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(Received 26 November 2003; published 7 July 2004)

A stochastic approach to the quantum dynamics randomly modulated in time by a discrete state non-Markovian noise, which possesses an arbitrary nonexponential distribution of the residence times, is developed. The formally *exact* expression for the Laplace-transformed quantum propagator averaged over the *stationary* realizations of such N-state non-Markovian noise is obtained. The theory possesses a wide range of applications. It includes some previous Markovian and non-Markovian theories as particular cases. In the context of the stochastic theory of spectral line shape and relaxation, the developed approach presents a non-Markovian generalization of the Kubo-Anderson theory of sudden modulation. In particular, the exact analytical expression is derived for the spectral line shape of optical transitions described by a Kubo oscillator with randomly modulated frequency which undergoes jumplike non-Markovian fluctuations in time.

DOI: 10.1103/PhysRevE.70.016109 PACS number(s): 05.40.−a, 76.20.+q

I. INTRODUCTION

The dynamics of classical and quantum systems in the presence of randomly fluctuating microfields of the environment presents one of the fundamental problems in physics. Spin relaxation in solids [1,2], exciton transport in molecular systems [3], single-molecular spectroscopy [4], and classical transport processes with fluctuating barriers [5] present a few relevant examples. A popular approach consists in modeling the ambient noise influence by means of a classical stochastic field acting on the dynamical system. In the case of quantum systems, such a phenomenological approach is known under the label of a stochastic Liouville equation (SLE) approach [7–9]. It is suitable in the limit of sufficiently high (formally infinite) temperatures [3,9]. In the field of chemical kinetics a similar methodology is known under the label of rate processes with dynamical disorder where the rates of chemical reactions fluctuate [6]. Moreover, the addition of a nonequilibrium classical noise into dissipative quantum dynamics can serve to describe the influence of the nonequilibrium environmental degrees of freedom on the transport properties [10].

The tractability of the SLE approach, which allows one to arrive at the exact model solutions in several known cases, has made it popular over the years. For example, the case of two-state quantum dynamics subjected to a white Gaussian noise can be treated exactly and the corresponding *exact* master equations for the averaged parameters of quantum systems can be derived [3,9]. However, already in the case of a colored Gaussian noise (the so-called colored noise problem) a perturbation theory must be used which leads generally to an approximate description—e.g., within a generalized master equation approach [11].

What to do, however, when the ambient noise has a non-Gaussian statistics and/or it does exhibit long-range, e.g., power law temporal correlations with a very large, practically infinite range? A relevant example is given by a $1/f^{\alpha}$ noise which is ubiquitous in the amorphous solids and other glasslike materials like proteins [12,13]. Any perturbation theory in such situations will certainly fail and we are confronted with a rather difficult problem. Nevertheless, for an arbitrary quantum dynamics the problem of finding the corresponding noise-averaged propagator can be solved exactly, at least formally, for a rather general class of non-Markovian jump processes modeled as a continuous-time random walk (CTRW) [14–16] within arbitrary, but finite number of states N. A similar problem has been already considered in several previous works, notably in Refs. [17,18]. These works did not solve, however, the problem at hand for the case of *stationary* noise averaging for a multistate non-Markovian noise, when the evolution of the considered stochastic process starts in the infinite past, and not simultaneously with the evolution of the considered dynamical system. In the case of a non-Markovian noise this problem is *not* trivial. Physically this is but the most important and relevant case to study.

In this work we utilize the most general description of the discrete state non-Markovian processes of the CTRW type with uncorrelated jumps. Generally, such processes are defined by the set of probability densities $\psi_{ij}(\tau)$ for making transitions among the discrete noise states [16]. The noise-averaged quantum propagator is obtained below for this general case. The approaches of Refs. [17] and [18] are unified within this general description. Next, the problem of stationary noise averaging is considered. It is shown in a constructive way how to make the stationary noise averaging in the case of factorized probability densities like in Ref. [18], but with the time-independent matrix of transition probabilities p_{ij}. In this respect, the present work is most close to Ref. [19], where a similar approach has been proposed; however, the explicit solution for the stationary noise-averaged quantum propagator has not been obtained. The corresponding formally *exact* expression for the Laplace-transform-averaged propagator is found in this work in the explicit form for the first time. This presents the *first* main result of

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this work which possesses an ample range of applications. In particular, the noise-averaged propagator of the Kubo oscillator with a stochastically modulated frequency, as well as the corresponding line shape form, is also obtained. This presents the *second* main result of this work which can be important, e.g., for the single-molecular spectroscopy.

II. MODEL AND THEORY

Let us consider an arbitrary quantum system with the Hamilton operator $\hat{H}[\xi(t)]$ which depends parametrically on the stochastic process $\xi(t)$ which in turn can acquire randomly in time N discrete values ξ_i. Accordingly, the Hamiltonian $\hat{H}[\xi(t)]$ can take on N different random operator values $\hat{H}[\xi_i]$. The discrete stochastic process is assumed to be a non-Markovian renewal process which is fully characterized by the set of probability densities $\psi_{ij}(\tau)$ which describe random transitions among the states ξ_i. Namely, $\psi_{ij}(\tau)$ is the probability density for making transition from the state j to the state i. These probability densities must obviously be positive and obey the normalization conditions

$$\sum_{i=1}^{N}\int_0^\infty \psi_{ij}(\tau)d\tau = 1, \tag{1}$$

for all $j=1,\ldots,N$. All random transitions are assumed to be mutually independent.[1] The residence time distribution (RTD) $\psi_j(\tau)$ in the state j reads obviously

$$\psi_j(\tau) = \sum_i \psi_{ij}(\tau). \tag{2}$$

The survival probability $\Phi_j(\tau)$ of the state j follows then as

$$\Phi_j(\tau) = \int_\tau^\infty \psi_j(\tau)d\tau. \tag{3}$$

This is the most general description used in the CTRW theory [16].

The problem is to average the quantum dynamics in the Liouville space which is characterized by the Liouville–von Neumann equation

$$\frac{d}{dt}\rho(t) = -i\mathcal{L}[\xi(t)]\rho(t) \tag{4}$$

for the density operator $\rho(t)$ over the realizations of noise $\xi(t)$. Here $\mathcal{L}[\xi(t)]$ in Eq. (4) stands for the quantum Liouville superoperator, $\mathcal{L}[\xi(t)](\cdot)=(1/\hbar)[\hat{H}[\xi(t)],(\cdot)]$. In other words, one has to find the noise-averaged propagator

$$\langle U(t_0+t,t_0)\rangle = \left\langle \mathcal{T}\exp\left[-i\int_{t_0}^{t_0+t}\mathcal{L}[\xi(\tau)]d\tau\right]\right\rangle, \tag{5}$$

where $\mathcal{T}$ denotes the time-ordering operator. It is the major advance of this work that we obtain the Laplace transform of propagator (5) in the *exact* form for *arbitrary non-Markovian processes* $\xi(t)$ *of the discussed form*. The results of previous research work done within the framework of SLE approach for the discrete Markovian processes [2] follow as a particular Markovian limit of the developed non-Markovian theory. Moreover, some previous non-Markovian theories, notably that by van Kampen [17] and that by Chvosta and Reineker [18], are also included as different interpretations of this general formulation.

In particular, the approach of van Kampen is reproduced by introduction of the time-dependent *age-specific* rates $k_{ij}(t)$ like in the renewal theory [20]. The probability densities $\psi_{ij}(\tau)$ then read[2] [17]

$$\psi_{ij}(\tau) := k_{ij}(\tau)\exp\left[-\sum_i\int_0^\tau k_{ij}(t)dt\right]. \tag{6}$$

The Markovian case corresponds to $k_{ij}(\tau)=\text{const}$. Any deviation of $\psi_{ij}(\tau)$ from the strictly exponential form which yields a time dependence of the transition rates $k_{ij}(\tau)$ amounts to a non-Markovian behavior.[3] Furthermore, the survival probability $\Phi_j(\tau)$ in the state j within the time-dependent rate description is given by

$$\Phi_j(\tau) = \exp\left[-\sum_{i=1}^{N}\int_0^\tau k_{ij}(t)dt\right] \tag{7}$$

and Eq. (6) then can be recast as

$$\psi_{ij}(\tau) := k_{ij}(\tau)\Phi_j(\tau). \tag{8}$$

The introduction of time-dependent rates is one possible way to describe the non-Markovian effects (see footnote 2). It is not unique. For example, Chvosta and Reineker adopted a quite different and more general standpoint [18]. Namely, they defined

[1]This is the so-called semi-Markov assumption. The term "semi-Markov," frequently used in the mathematical literature, is, however, somewhat unfortunate. It comes from a generalization of the discrete time Markovian chain processes to the continuous time case. Such continuous time processes are, however, generally non-Markovian since the statistical independence of the residence time intervals does not imply yet that all the multitime joint probability distributions for the considered process can be factorized through the corresponding two-time conditional and single-time probability distributions.

[2]Note that such a time dependence of $k_{ij}(\tau)$ has nothing to do with the possible nonstationarity invoked—e.g., due to the action of external fields like in the problem of stochastic resonance (SR) [21]. Introducing such time-dependent rates is merely a language to describe the non-Markovian memory effects. In the case of a nonstationary background noise driven by a time-dependent signal (like in the non-Markovian SR problem; cf. [22]) the use of such language in a non-Markovian situation should be avoided as it can potentially confuse the reader.

[3]This observation can be rationalized as follows. Let us consider a sojourn in the state j characterized by the survival probability $\Phi_j(\tau)$. The corresponding residence time interval $[0,\tau]$ can be arbitrarily divided into two pieces $[0,\tau_1]$ and $[\tau_1,\tau]$. If no memory effects are present, then $\Phi_j(\tau)=\Phi_j(\tau-\tau_1)\Phi_j(\tau_1)$. The only nontrivial solution of this latter functional equation which decays in time reads $\Phi_j(\tau)=\exp(-\gamma_j\tau)$, with $\gamma_j>0$. This corresponds to a Markovian case.

$$\psi_{ij}(\tau):=p_{ij}(\tau)\psi_j(\tau), \tag{9}$$

with $\sum_i p_{ij}(\tau)=1$. The interpretation is as follows. The process stays in the state j during a random time interval characterized by the probability density $\psi_j(\tau)$. At the end of this time interval the process makes jump into the state i with a generally time-dependent conditional probability $p_{ij}(\tau)$. Indeed, any stochastic process of the considered kind can be interpreted in this way. For some particular applications in [18] the probability densities $\psi_j(\tau)$ were taken strictly exponential and all the non-Markovian effects were assumed to come from the *time-dependent* transition probabilities $p_{ij}(\tau)$. By equating Eqs. (8) and (9) and taking into account that $\psi_j(\tau):=-d\Phi_j(\tau)/d\tau$ it is easy to see that the van Kampen approach can be reduced to that of Chvosta and Reineker with the time-dependent transition probabilities

$$p_{ij}(\tau)=\frac{k_{ij}(\tau)}{\sum_i k_{ij}(\tau)} \tag{10}$$

and with the nonexponential probability densities $\psi_j(\tau)$ which follow as $\psi_j(\tau)=\gamma_j(\tau)\exp[-\int_0^\tau \gamma_j(t)dt]$ with $\gamma_j(\tau):=\sum_i k_{ij}(\tau)$.

The description of non-Markovian effects with the time-dependent transition probabilities $p_{ij}(\tau)$ seems, however, be merely a theoretical device. It appears to be rather difficult (if possible) to obtain $p_{ij}(\tau)$ from the sample trajectories of an experimentally *observed* random process $\xi(t)$. In view of Eq. (10) the same is valid for the concept of time-dependent rates. These rates cannot be measured directly from the sample trajectories. On the contrary, the RTD $\psi_j(\tau)$ and the *time-independent* p_{ij} (with $p_{ii}:=0$, which is assumed in the following) can be routinely deduced from the sample trajectories measured in a *single-molecular* experiment. This latter description is definitely more advantageous from the practical point of view. From the experimentally well-defined quantities $\Phi_j(\tau)$ and p_{ij}, the corresponding time-dependent rates description can be readily found as

$$k_{ij}(\tau)=-p_{ij}\frac{d\ln[\Phi_j(\tau)]}{d\tau}. \tag{11}$$

Moreover, as will be shown below, this description with constant p_{ij} in Eq. (9) does provide a consistent way in order to construct the *stationary* realizations of the *non-Markovian* process $\xi(t)$ and, therefore, in order to find $\langle U(t)\rangle$ averaged, correspondingly, over the *stationary* realizations of $\xi(t)$. These circumstances give definite advantages of the approach with factorized $\psi_{ij}(\tau)$ and *time-independent* p_{ij} as compare with the formulations in [17,18], even though the technical details are quite similar. The correct quantum-mechanical propagator averaged over the *stationary* realizations of a *non-Markovian* discrete-state noise with an arbitrary number of states is obtained in this work for the first time. This corresponds to the situation where the quantum system was prepared at the time t_0 in a nonequilibrium state described by the density matrix $\rho(t_0)$, but the noise was not specially prepared but it has been already relaxed to its stationary state. The ambient noise evolution was started in the infinite past and one assumes that the initial preparation of the quantum system in a nonequilibrium state has no influence on the noise source. This is the most important physical situation to confront with.

The task of performing the noise averaging of the quantum dynamics in Eq. (5) can be solved exactly due the piecewise constant character of the noise $\xi(t)$ [23,24]. Namely, let us consider the time interval $[t_0,t]$ and to take a frozen realization of $\xi(t)$ assuming k switching events within this time interval at the time instants t_i:

$$t_0<t_1<t_2<\cdots<t_k<t. \tag{12}$$

Correspondingly, the noise takes on the values $\xi_{j_0},\xi_{j_1},\ldots,\xi_{j_k}$ in the time sequel. Then, the propagator $U(t,t_0)$ reads obviously

$$U(t,t_0)=e^{-i\mathcal{L}[\xi_{j_k}](t-t_k)}e^{-i\mathcal{L}[\xi_{j_{k-1}}](t_k-t_{k-1})}\cdots e^{-i\mathcal{L}[\xi_{j_0}](t_1-t_0)}. \tag{13}$$

Let us assume first that it is known with certainty that at the time instant t_0 the process $\xi(t)$ has *just started* its sojourn in the state j_0. In other words, the process $\xi(t)$ has been *prepared* in the state j_0 at t_0. Then, the corresponding k-times conditional probability density for such noise trajectory realization is

$$P_k(\xi_{j_k},t_k;\xi_{j_{k-1}},t_{k-1};\ldots;\xi_{j_1},t_1|\xi_{j_0},t_0)$$
$$=\Phi_{j_k}(t-t_k)\psi_{j_kj_{k-1}}(t_k-t_{k-1})\cdots\psi_{j_1j_0}(t_1-t_0). \tag{14}$$

In order to obtain the noise-averaged $\langle U(t,t_0)\rangle_{j_0}$ conditioned on such *nonstationary* initial noise preparation one has to average Eq. (13) with the probability measure in Eq. (14) (for $k=0,\ldots,\infty$). Literally (operationally) this means the following. First, one has to construct the time-ordered product of Eqs. (13) and (14)—i.e.,

$$\Phi_{j_k}(t-t_k)e^{-i\mathcal{L}[\xi_{j_k}](t-t_k)}\psi_{j_kj_{k-1}}(t_k-t_{k-1})e^{-i\mathcal{L}[\xi_{j_{k-1}}](t_k-t_{k-1})}\ldots$$
$$\times\psi_{j_1j_0}(t_1-t_0)e^{-i\mathcal{L}[\xi_{j_0}](t_1-t_0)}. \tag{15}$$

Second, one has to perform the k-dimensional time integration of Eq. (15) over the variables $\{t_k\}$ within the time-ordered domain (12) and to sum the results over all possible $\{j_k\}$. Furthermore, this procedure has to be repeated for every $k=0,\ldots,\infty$ and the results summed at the end. The case $k=0$ is special with

$$P_0(\xi_{j_0},t_0)=\Phi_{j_0}(t-t_0). \tag{16}$$

The just outlined task can be easily done formally by use of the Laplace transform, denoted in the following as $\tilde{A}(s):=\int_0^\infty\exp(-s\tau)A(\tau)d\tau$ for any time-dependent quantity $A(\tau)$. For this goal, let us introduce two auxiliary matrix operators $\tilde{A}(s)$ and $\tilde{B}(s)$ with the matrix elements

$$\tilde{A}_{kl}(s):=\delta_{kl}\int_0^\infty\Phi_l(\tau)e^{-(s+i\mathcal{L}[\xi_l])\tau}d\tau \tag{17}$$

and

$$\widetilde{B}_{kl}(s):=\int_0^\infty \psi_{kl}(\tau)e^{-(s+i\mathcal{L}[\xi_l])\tau}d\tau, \tag{18}$$

correspondingly. Then all what remains to do is to sum the geometric matrix operator series. The result reads,

$$\langle\widetilde{U}(s)\rangle_{j_0}=\sum_i \{\widetilde{A}(s)[I-\widetilde{B}(s)]^{-1}\}_{ij_0}, \tag{19}$$

where I is the unity matrix. It is quite obvious that instead of the quantum Liouville operator in Eq. (4) there could be any linear operator—e.g., $\mathcal{L}$ could be a matrix and $\rho(t)$ could be then a vector function. Then, the developed theory can be immediately applied to the averaging of arbitrary linear stochastic differential equations [24,25]. Even nonlinear stochastic differential equations can be attempted to deal with by introducing a Liouville equation for the corresponding classical probability density [25]. The earlier results in [17] and [18] are reproduced immediately from Eqs. (17)–(19) by an appropriate modification of the considered problem and specifying the transition probability densities $\psi_{ij}(\tau)$ from a most general (nonfactorized form) to a particular representation in accordance with the above discussion.

The derived result in Eqs. (17)–(19) corresponds to the initial preparation of $\xi(t)$ in a particular state j_0. Experimentally, this presents a quite unusual and strongly nonequilibrium situation. For a stationary environment one has to perform yet an additional averaging of $\langle\widetilde{U}(s)\rangle_{j_0}$ over the initial distribution $p_{j_0}(t_0)$ taken as the stationary distribution—i.e., $p_{j_0}(t_0)=p^{st}_{j_0}$, where $p^{st}_j=\lim_{t\to\infty}p_j(t)$. Indeed, this presents a valid prescription for stationary noise averaging in the Markovian case. However, in a non-Markovian case this prescription is not sufficient.

Quite generally, the stationarity of noise realizations in the strict sense requires [25] that not only the single-time distribution $p_j(t)$, but also all the multitime joint probability distributions of the given process must be invariants of a simultaneous time shift of all time arguments. However, for many physical applications, the stationarity in a weak sense—i.e., on the level of the two-time $P(j,t;j_0,t_0)$ joint distribution—is sufficient. Then, e.g., the stationary power spectrum of the corresponding process can be defined. This two-time joint distribution can be expressed as $P(j,t;j_0,t_0)=\Pi_{jj0}(t|t_0)p_{j0}(t_0)$ via the conditional probabilities $\Pi_{jj0}(t|t_0)$ (propagator of the process). For a stationary process the consistency condition, $p^{st}_j=\Sigma_{j0}\Pi_{jj0}(t|t_0)p^{st}_{j0}$, must be satisfied for all times; i.e., p^{st}_j has to be the fixed point of the corresponding propagator (see the Appendix). The propagator of the non-Markovian process having this property can be called quasistationary. In the present case, in order to construct such a propagator and the corresponding stationary realizations of the noise trajectories the probability density of the *first* time intervals must differ from the all subsequent ones. Indeed, if a noise state j was occupied at $t=t_0$ with the stationary probability p^{st}_j, it is not known for how long this state was already occupied *before* t_0. The proper conditioning on and averaging over this unknown time must be made and the corresponding survival probabilities for the *first* residence time interval $\tau_0=t_1-t_0$ be introduced.[4] These survival probabilities read[5] [20]

$$\Phi^{(0)}_j(\tau)=\frac{\int_\tau^\infty \Phi_j(\tau')d\tau'}{\langle\tau_j\rangle}, \tag{20}$$

where $\langle\tau_j\rangle=\int_0^\infty \Phi_j(\tau)d\tau$ is the mean residence time (MRT) of the noise in the state j. Only for strictly exponential survival probabilities—i.e., in the Markovian case—$\Phi^{(0)}_j(\tau)=\Phi_j(\tau)$. Otherwise, this is not the case. The corresponding residence time distributions follow immediately as the negative time derivative of $\Phi^{(0)}_j(\tau)$ in Eq. (20) and are known to be [15,20]

$$\psi^{(0)}_j(\tau)=\frac{\Phi_j(\tau)}{\langle\tau_j\rangle}. \tag{21}$$

The *first time* transition densities $\psi^{(0)}_{ij}(\tau)$ then follow as

$$\psi^{(0)}_{ij}(\tau)=p_{ij}\frac{\Phi_j(\tau)}{\langle\tau_j\rangle}. \tag{22}$$

For the logical consistency of this definition with the consideration pursued in footnote 4, p_{ij} *must be* time-independent constants. Otherwise, a logical problem emerges: How to make the proper conditioning of $p_{ij}(\tau)$ on the unknown times before t_0? This is the reason why within the approaches of time-dependent $p_{ij}(\tau)$ or time-dependent rates $k_{ij}(\tau)$ it is rather obscure how to solve the problem of stationary noise averaging. Therefore, these approaches do not seem suit well for this stated purpose.

In accord with the above discussion, the transition density $\psi_{j_1j_0}(t_1-t_0)$ in Eq. (14) must be replaced by $\psi^{(0)}_{j_1j_0}(t_1-t_0)$ from Eq. (22). Moreover, $\Phi_{j_0}(t-t_0)$ in Eq. (16) must be replaced by $\Phi^{(0)}_{j_0}(t-t_0)$ from Eq. (20). To account for these modifications, two auxiliary quantities $\widetilde{A}^{(0)}_{kl}(s)$ and $\widetilde{B}^{(0)}_{kl}(s)$ are introduced which are given by the expressions similar to Eqs. (17) and (18), but with $\Phi^{(0)}_j(\tau)$ instead of $\Phi_j(\tau)$ and $\psi^{(0)}_{ij}(\tau)$ instead of $\psi_{ij}(\tau)$—i.e.,

[4]A clear-cut proof of this fact was presented in many works; see, e.g., [15,22]. We reproduce it here for the reader's convenience. Indeed, it is not known for how long the initial state $\xi(t_0)$ was already occupied *before* the observation started at $t_0=0$. Without loss of generality, let us assume $\xi(0)=\xi_j$ and the unknown time elapsed before $t_0=0$ was τ^*. Then, the actual survival probability at $t=\tau_0$ is $\Phi_j(\tau^*+\tau_0)$. On the other hand, $\Phi_j(\tau^*+\tau_0)=\Phi_j(\tau_0|\tau^*)\Phi_j(\tau^*)$, where the corresponding *conditional* survival probability $\Phi_j(\tau_0|\tau^*)$ is introduced. This latter relation serves just as a definition for $\Phi_j(\tau_0|\tau^*)$. In the Markovian case $\Phi_j(\tau_0|\tau^*)=\Phi_j(\tau_0)$. To obtain the survival probability of the first time interval $\Phi^{(0)}_j(\tau_0)$, one must average $\Phi_j(\tau_0|\tau^*)$ over the probability density of τ^* which is $p_j(\tau^*)=\Phi_j(\tau^*)/\int_0^\infty\Phi_j(t)dt$. Therefore, $\Phi^{(0)}_j(\tau_0):=\int_0^\infty \Phi_j(\tau_0|\tau^*)p_j(\tau^*)d\tau^*$. Proceeding along these lines, the important relation (20) follows immediately.

[5]Note that no averaging over the unknown times τ^* (see footnote 4) was made in [17] (see Appendix C there). Therefore, the problem of stationary noise averaging was not solved in this important paper.

$$\widetilde{A}^{(0)}_{kl}(s) := \frac{\delta_{kl}}{\langle\tau_l\rangle}\int_0^\infty e^{-(s+i\mathcal{L}[\xi_l])\tau}\int_\tau^\infty \Phi_l(\tau')d\tau' d\tau \quad (23)$$

and

$$\widetilde{B}^{(0)}_{kl}(s) := \frac{p_{kl}}{\langle\tau_l\rangle}\int_0^\infty \Phi_l(\tau)e^{-(s+i\mathcal{L}[\xi_l])\tau}d\tau = \frac{p_{kl}}{\langle\tau_l\rangle}\widetilde{A}_{ll}(s). \quad (24)$$

The resulting geometric operator series can again be easily summed exactly. For the (stationary) noise-averaged Laplace-transformed propagator $\langle\widetilde{U}(s)\rangle$ we obtain

$$\langle\widetilde{U}(s)\rangle = \sum_{ij}\{\widetilde{A}^{(0)}(s) + \widetilde{A}(s)[I-\widetilde{B}(s)]^{-1}\widetilde{B}^{(0)}(s)\}_{ij}p_j^{st}, \quad (25)$$

where

$$p_j^{st} = \frac{\langle\tau_j\rangle}{\sum_k \langle\tau_k\rangle} \quad (26)$$

are the stationary occupation probabilities of ξ_j [see Eq. (A10) in the Appendix and the corresponding discussion]. This result can be brought into a physically more insightful form by using the identity $\int_\tau^\infty \Phi_j(\tau')d\tau' = \langle\tau_j\rangle - \int_0^\tau \Phi_j(\tau')d\tau'$ and upon introducing two new auxiliary quantities

$$\widetilde{C}_{kl}(s) := \delta_{kl}\int_0^\infty e^{-(s+i\mathcal{L}[\xi_l])\tau}\int_0^\tau \Phi_l(\tau')d\tau' d\tau \quad (27)$$

and

$$\widetilde{D}_{kl}(s) := \delta_{kl}\int_0^\infty \psi_l(\tau)e^{-(s+i\mathcal{L}[\xi_l])\tau}d\tau. \quad (28)$$

Finally we obtain

$$\langle\widetilde{U}(s)\rangle = \langle\widetilde{U}(s)\rangle_{static} - \frac{1}{T}\sum_{ij}\{\widetilde{C}(s) - \widetilde{A}(s)[I-P\widetilde{D}(s)]^{-1}P\widetilde{A}(s)\}_{ij}, \quad (29)$$

where $\langle\widetilde{U}(s)\rangle_{static}$ is the Laplace transform of the statically averaged propagator,

$$\langle U(\tau)\rangle_{static} := \sum_k e^{-i\mathcal{L}[\xi_k]\tau}p_k^{st}, \quad (30)$$

$T=\Sigma_k \langle\tau_k\rangle$ is the sum of mean residence times, and P is the matrix of transition probabilities p_{ij} ["scattering matrix" of the random process $\xi(t)$]. The result in Eqs. (29) and (30) together with Eqs. (17), (27), and (28) presents the cornerstone result of this work which can be used in numerous applications.

III. APPLICATION: KUBO OSCILLATOR

As a simplest practical example we consider the averaging of the so-called Kubo oscillator

$$\dot{x}(t) = i\omega[\xi(t)]x(t). \quad (31)$$

This particular problem appears in the theory of optical line shapes, in the nuclear magnetic resonance [1,2], and in the single-molecular spectroscopy [4]. In Eq. (31), $\omega[\xi(t)]$ presents a stochastically modulated frequency of quantum transitions between the levels of a "two-state atom" or between the eigenstates of a spin 1/2 which are caused by the action of a resonant laser or magnetic field, respectively. The spectral line shape is determined through the corresponding stochastically averaged propagator of Kubo oscillator as [2]

$$I(\omega) = \frac{1}{\pi}\lim_{\epsilon\to+0}\mathrm{Re}[\widetilde{U}(i\omega+\epsilon)]. \quad (32)$$

Note that the limit $\epsilon\to+0$ in Eq. (32) is necessary for the regularization of the corresponding integral in the quasistatic limit $T\to\infty$. By identifying $\mathcal{L}[\xi_k]$ with $-\omega_k$ in Eq. (29) we obtain after some algebra

$$\langle\widetilde{U}(s)\rangle = \sum_k \frac{p_k^{st}}{s-i\omega_k} - \frac{1}{\sum_k\langle\tau_k\rangle}\sum_k \frac{1-\widetilde{\psi}_k(s-i\omega_k)}{(s-i\omega_k)^2} + \frac{1}{\sum_k\langle\tau_k\rangle}\sum_{n,l,m}\frac{1-\widetilde{\psi}_l(s-i\omega_l)}{s-i\omega_l}\left(\frac{1}{I-P\widetilde{D}(s)}\right)_{lm} \times p_{mn}\frac{1-\widetilde{\psi}_n(s-i\omega_n)}{s-i\omega_n}, \quad (33)$$

with $\widetilde{D}_{nm}(s) = \delta_{nm}\widetilde{\psi}_m(s-i\omega_m)$. The corresponding line shape follows immediately from Eq. (33) by virtue of Eq. (32). This result presents a non-Markovian generalization of the earlier result by Kubo [2] for arbitrary N-state discrete Markovian processes. The generalization consists in allowing for arbitrary non-exponential RTD's $\psi_k(\tau)$ or, equivalently, in accordance with Eq. (11) for time-dependent transition rates $k_{ij}(\tau)$. This generalization is obtained here for the first time and presents one of our main results. Let us further simplify the result in Eq. (33) for the case of two-state non-Markovian noise with $p_{12}=p_{21}=1$. Then, Eq. (33) yields after some simplifications

$$\langle\widetilde{U}(s)\rangle = \sum_{k=1,2}\frac{1}{s-i\omega_k}\frac{\langle\tau_k\rangle}{\langle\tau_1\rangle+\langle\tau_2\rangle} + \frac{(\omega_1-\omega_2)^2}{(\langle\tau_1\rangle+\langle\tau_2\rangle)(s-i\omega_1)^2(s-i\omega_2)^2} \times \frac{[1-\widetilde{\psi}_1(s-i\omega_1)][1-\widetilde{\psi}_2(s-i\omega_2)]}{1-\widetilde{\psi}_1(s-i\omega_1)\widetilde{\psi}_2(s-i\omega_2)}. \quad (34)$$

With Eq. (34) in Eq. (32) one obtains the result for the corresponding spectral line shape which is equivalent to one obtained recently in Ref. [26] using a different method. It is reproduced here as a simplest application of our more general approach.

IV. SUMMARY

In this work the problem of the stochastic averaging of a quantum dynamics with non-Markovian fluctuating parameters has been investigated within the trajectory description of continuous time random walk theory. The formally exact expression for the stochastically averaged quantum-mechanical propagator is obtained for the most general CTRW with uncorrelated jumps and for a nonequilibrium noise preparation. The problem of stationary noise averaging has been solved for the practically relevant formulation with the time-independent matrix of transition probabilities p_{ij}. Especially, the formally exact expression for the stationary averaged quantum propagator has been found in an explicit form. This general expression has been used on order to find the stationary propagator of the Kubo oscillator describing the spectral line shape of optical transitions in a two-state atom. Further applications, such as decoherence of a two-state quantum dynamics driven by two-state non-Markovian noises, including $1/f^{\alpha}$ noise case, are in progress.

ACKNOWLEDGMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich SFB-486, "Manipulation of matter on the nanoscale," Project No. A10.

APPENDIX: PROPAGATORS AND GENERALIZED MASTER EQUATIONS

In this appendix, both the nonstationary propagator and the propagator for quasistationary initial preparations for the considered non-Markovian processes are obtained, along with the corresponding generalized master equations (GME's). The propagator Π_{ij} of the process $\xi(t)$ or the matrix of conditional probabilities connects the initial probability vector $\vec{p}(t_0)$ with the final one, $\vec{p}(t_0+\tau)$—i.e.,

$$p_i(t_0+\tau) = \sum_j \Pi_{ij}(t_0+\tau|t_0)p_j(t_0). \tag{A1}$$

The expression for the Laplace transform $\tilde{\Pi}_{ij}(s)$ can be obtain in a way similar to the averaging of quantum propagator in Eqs. (19) and (25). Basically, one has to put there $\mathcal{L}\to 0$. For the nonstationary propagator of $\xi(t)$—i.e., when the process $\xi(t)$ *starts* its evolution at $t=t_0$ in a particular state—the result reads for the general case of nonfactorized probability densities $\psi_{ij}(\tau)$ as follows:

$$\tilde{\Pi}_{ij}(s) = \tilde{\Phi}_i(s)\{[I-\tilde{\Psi}(s)]^{-1}\}_{ij}, \tag{A2}$$

where Ψ is the matrix of $\tilde{\psi}_{ij}(s)$ and $\tilde{\Phi}_j(s)=[1-\tilde{\psi}_j(s)]/s$, $\tilde{\psi}_j(s)=\Sigma_i\,\tilde{\psi}_{ij}(s)$. For quasistationary initial preparations the propagator of the non-Markovian process is generally different [22,27]. In the factorized case $\psi_{ij}(\tau)=p_{ij}\psi_j(\tau)$ it reads for the considered process [cf. Eq. (25)]:

$$\tilde{\Pi}^{st}_{ij}(s) = \tilde{\Phi}^{(0)}_i(s)\delta_{ij} + \tilde{\Phi}_i(s)\sum_k \{[I-\tilde{\Psi}(s)]^{-1}\}_{ik}p_{kj}\frac{\tilde{\Phi}_j(s)}{\langle\tau_j\rangle}, \tag{A3}$$

where $\tilde{\Phi}^{(0)}_j(s)=1/s-[1-\tilde{\psi}_j(s)]/(s^2\langle\tau_j\rangle)$. The stationary populations follow as $p_i^{st}=\lim_{s\to 0}[s\tilde{\Pi}_{ij}(s)]$. The quasistationary propagator $\Pi^{st}_{ij}(\tau|0)$ must satisfy the consistency condition $p_i^{st}=\Sigma_j\,\Pi^{st}_{ij}(\tau|0)p_j^{st}$ for all times τ; i.e., $\vec{p}^{st}$ is the fixed point of $\Pi^{st}_{ij}(\tau|0)$. Let us prove this fact and find p_i^{st}. It is more convenient to do both tasks by finding first the corresponding GME's for $p_i(t)$. These generalized master equations are of substantial interest *per se*.

In order to find the corresponding GME's the procedure of [19] can be applied to a more general present case of nonfactorized $\psi_{ij}(\tau)$. Indeed, let us consider the conditional probability $P_k(j|j_0)(t)$ for making k jumps within the time interval $[0,t]$ starting at $t=0$ in the state j_0 with the probability $p_{j_0}(0)$ and finishing in the state j with the probability $p_j(t)$. This probability is given by a corresponding k-dimensional integral of Eq. (14) [see the discussion below Eq. (14)] with the summation made over $j_{k-1},j_{k-2},\ldots,j_1$. The corresponding Laplace transform $\tilde{P}^{(k)}_{jj_0}(s)$ reads

$$\tilde{P}^{(k)}_{jj_0}(s) = \sum_{j_{k-1}}\cdots\sum_{j_1}\tilde{\Phi}_j(s)\tilde{\psi}_{jj_{k-1}}(s)\cdots\tilde{\psi}_{j_2j_1}(s)\tilde{\psi}^{(0)}_{j_1j_0}(s) \tag{A4}$$

for $k>0$. Here, Eq. (14) was used in a slightly modified form with $\psi^{(0)}_{ij}(\tau)$ for the probability densities of the first time intervals. Furthermore, for $k=0$, $\tilde{P}^{(0)}_{jj_0}(s)=\tilde{\Phi}^{(0)}_j(s)\delta_{jj_0}$, where $\tilde{\Phi}^{(0)}_j(s)$ is the Laplace transform of the corresponding survival probability $\Phi^{(0)}_j(\tau)=\Sigma_i\int_\tau^\infty\psi^{(0)}_{ij}(\tau')d\tau'$ of the first time interval. For $k\geqslant 2$, the quantities $\tilde{P}^{(k)}_{jj_0}(s)$ satisfy obviously the following recurrence relation:

$$\tilde{P}^{(k)}_{jj_0}(s) = \tilde{\Phi}_j(s)\sum_n\tilde{\psi}_{jn}(s)\frac{\tilde{P}^{(k-1)}_{nj_0}(s)}{\tilde{\Phi}_n(s)}. \tag{A5}$$

Furthermore, the Laplace transform of propagator $\tilde{\Pi}_{jj_0}(s)$ is expressed in terms of $\tilde{P}^{(k)}_{jj_0}(s)$ as $\tilde{\Pi}_{jj_0}(s)=\Sigma_{k=0}^\infty\,\tilde{P}^{(k)}_{jj_0}(s)$. Then, by virtue of Laplace-transformed equation (A1) with $t_0=0$,

$$\begin{aligned}\sum_{k=2}^{\infty}\sum_{j_0}\tilde{P}^{(k)}_{jj_0}(s)p_{j_0}(0) &= \tilde{p}_j(s) - \sum_{j_0}\tilde{P}^{(1)}_{jj_0}(s)p_{j_0}(0) - \tilde{P}^{(0)}_{jj}(s)p_j(0)\\ &= \tilde{\Phi}_j(s)\sum_n\tilde{\psi}_{jn}(s)\frac{1}{\tilde{\Phi}_n(s)}\sum_{k=2}^{\infty}\sum_{j_0}\tilde{P}^{(k-1)}_{nj_0}(s)\\ &\quad\times p_{j_0}(0),\end{aligned} \tag{A6}$$

where the recurrence relation (A5) has been used. The use of $\Sigma_{k=2}^\infty\,\Sigma_{j_0}\,\tilde{P}^{(k-1)}_{nj_0}(s)p_{j_0}(0)=\tilde{p}_n(s)-\tilde{\Phi}^{(0)}_n(s)p_n(0)$ in Eq. (A6) finally yields

$$\begin{aligned}\tilde{p}_j(s) &= \tilde{\Phi}_j(s)\sum_n\tilde{\psi}_{jn}(s)\frac{\tilde{p}_n(s)}{\tilde{\Phi}_n(s)} + \tilde{\Phi}^{(0)}_j(s)p_j(0)\\ &\quad+\tilde{\Phi}_j(s)\sum_n\left(\tilde{\psi}^{(0)}_{jn}(s) - \tilde{\psi}_{jn}(s)\frac{\tilde{\Phi}^{(0)}_n(s)}{\tilde{\Phi}_n(s)}\right)p_n(0).\end{aligned} \tag{A7}$$

Let us consider now the case when the noise has been prepared at $t_0=0$ in a particular state with the probability one. Then, $\psi_{ij}^{(0)}(\tau)\equiv\psi_{ij}(\tau)$ and the last term in Eq. (A7) vanishes. For this class of nonequilibrium initial preparations, the inversion of Eq. (A7) yields

$$\dot{p}_j(t)=-\sum_n\int_0^t \Gamma_{nj}(t-t')p_j(t')dt' + \sum_n\int_0^t \Gamma_{jn}(t-t')p_n(t')dt', \qquad (A8)$$

where the Laplace-transformed kernels reads

$$\tilde{\Gamma}_{jn}(s)=\frac{s\tilde{\psi}_{jn}(s)}{1-\tilde{\psi}_n(s)}, \qquad (A9)$$

with $\tilde{\psi}_n(s)=\Sigma_j\,\tilde{\psi}_{jn}(s)$. The just derived GME (A8) and (A9) is the most general GME for the continuous time random walk processes with uncorrelated jumps for the given class of initial preparations. In the case of factorized (but still non-separable) CTRW with $\psi_{ij}(\tau)=p_{ij}\psi_j(\tau)$ it reduces to the GME of Burstein, Zharikov, and Temkin [19]. Moreover, with the assumption that all $\psi_j(\tau)$ are equal (separable CTRW of Montroll and Weiss), it reduces further to the GME of Kenkre, Montroll, and Shlesinger [28]. The stationary populations can be obtained from Eq. (A7) as $p_j^{st}=\lim_{s\to 0}[s\tilde{p}_j(s)]$. Assuming that the mean residence times $\langle\tau_j\rangle$ exist—i.e., $\tilde{\psi}_{ij}(s)=\alpha_{ij}-st_{ij}+o(s)$ with $\Sigma_i\,\alpha_{ij}=1$ and $\Sigma_i\,t_{ij}=\langle\tau_j\rangle$— Eq. (A7) yields the system of linear algebraic equations for the stationary populations:

$$\frac{p_j^{st}}{\langle\tau_j\rangle}=\sum_n \alpha_{jn}\frac{p_n^{st}}{\langle\tau_n\rangle}. \qquad (A10)$$

For an ergodic process the stationary probability to find the process in a particular state should be proportional to the time which the process spends in this particular state on average—i.e., be given by Eq. (26). It is easy to verify that Eq. (26) provides the solution of Eq. (A10) for $\Sigma_j\,\alpha_{ij}=1$ (for the factorized case α_{ij} coincide obviously with p_{ij}). This latter condition can be also expressed as

$$\sum_{j=1}^{N}\int_0^\infty \psi_{ij}(\tau)d\tau=1. \qquad (A11)$$

For factorized case $\psi_{jn}(\tau)=p_{jn}\psi_n(\tau)$ with $\psi_j^{(0)}(\tau)=\Phi_j(\tau)/\langle\tau_j\rangle$ (see footnote[4]), the inversion of Eq. (A7) yields the GME for the discussed non-Markovian process with quasistationary initial preparations:

$$\dot{p}_j(t)=-\int_0^t \Gamma_j(t-t')[p_j(t')-p_j(0)]dt'+\sum_n p_{jn}\int_0^t \Gamma_n(t-t')\times[p_n(t')-p_n(0)]dt'-\frac{p_j(0)}{\langle\tau_j\rangle}+\sum_n p_{jn}\frac{p_n(0)}{\langle\tau_n\rangle}, \qquad (A12)$$

with the kernels given by $\tilde{\Gamma}_j(s)=s\tilde{\psi}_j(s)/[1-\tilde{\psi}_j(s)]$. By choosing $p_n(0)=p_n^{st}$ which satisfy Eq. (A10) it becomes obvious that $p_n(t)=p_n^{st}$ is the solution of Eq. (A12) for *all* times $t>0$. This means that the stationary $\vec{p}^{st}$ provides indeed the fixed point of the corresponding quasistationary propagator.

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