# A static ensemble approximation for stochastically modulated quantum systems

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A short-time approximation for the evolution of quantum systems governed by a Hamiltonian with stochastic time dependence is derived. The evolution operator of the system is replaced by an ensemble of evolution operators with time-independent Hamiltonians, weighted by a distribution function related to the "line shape function" of a randomly modulated harmonic oscillator. The approximation conserves the trace of the density matrix and converges to the exact solution in the case of very slow and in the case of very rapid stochastic modulation. The approximation is applied to hyperfine-induced singlet–triplet transitions of a biradical-like system with fluctuating exchange interaction.

## I. INTRODUCTION

In this article we consider stochastic quantum systems described by a Hamiltonian

$$H(t) = f(t)D' + A', \tag{1.1}$$

where $D'$ and $A'$ are time-independent operators, and $f(t)$ describes random fluctuations. We assume the random process $f(t)$ to be stationary, Markovian, and ergodic.[1] $D'$ is assumed to have only two distinct (possibly degenerate) eigenvalues. $A'$ is an arbitrary operator and does not commute with $D'$. The off-diagonal elements of $A'$, in a basis where $D'$ is diagonal, introduce transitions between the eigenstates of $D'$ and define the perturbation operator $A$, i.e., $A = A' - \mathrm{diag}(A'_{11}, A'_{22}, \ldots)$. Systems governed by fluctuating Hamiltonians like Eq. (1.1) can be described by a stochastic Liouville equation.[2–5] The numerical solution of this equation, in case that the number of realizations $f_k$ of $f(t)$ is large [$f(t) \in \{f_k, k = 1,2,\ldots,n\}$ assuming a discrete process], consumes enormous computational resources and does not reveal much physical insight.

The stochastic process which we assume to govern the fluctuations of $f(t)$ is described by a master equation or by a Fokker–Planck equation in the case that the realizations of $f(t)$ are taken from a discrete or a continuous set, respectively.[1] In either case the evolution of the stochastic process can be cast into an equation of the type

$$\partial_t \mathbf{q}(t) = \mathbf{l}\mathbf{q}(t), \tag{1.2}$$

where $\mathbf{l}$ is a matrix (master equation, discrete process) or a differential operator (Fokker–Planck equation, continuous process). $\mathbf{q}$ represents a vector, i.e., $\mathbf{q}^T = [q_1(t), q_2(t), \ldots, q_n(t)]$ or a function, i.e., $\mathbf{q} = q(f,t)$, which gives the probability that a certain realization of $f$ occurs at time $t$. Since (1.2) is assumed to describe a stationary, ergodic process $\mathbf{l}$ posesses a unique eigenvector (eigenfunction) to the eigenvalue zero

$$\mathbf{l}\mathbf{p} = 0, \tag{1.3}$$

where $\mathbf{p}$ is the equilibrium probability of $f$ and is, like $\mathbf{q}$, either a vector, i.e., $\mathbf{p}^T = (p_1, \ldots, p_n)$, or a function, i.e., $\mathbf{p} = p(f)$.

For the time evolution of systems governed by random Hamiltonians of the particular form of Eq. (1.1) we will derive an approximation in which the system is described by an ensemble of time-independent Hamiltonians $H(j) = jD' + A'$ with distribution $I(j)$, $j \in \mathbf{R}$. The distribution function $I(j)$ is related to the line shape function of a randomly modulated harmonic oscillator.[6] This "static ensemble approximation" computationally is more easily managable than the original problem and through $I(j)$ provides an interesting physical interpretation of the stochastic quantum system. The main features of the approximation are:

(i) The approximation is exact to third order in the perturbation operator $A$, when the initial density matrix $\rho_0 = \rho(t = 0)$ satisfies $[D', \rho_0] = 0$.

(ii) In the case of very rapid or very slow stochastic motion the approximation converges to the exact solution.

(iii) The approximation reproduces the trace of the density matrix, i.e., total probability, exactly.

The approximation suggested describes the exact evolution operator for the density matrix to Eq. (1.1) by an infinite series in the perturbation operator $A$; the truncation of the series to third order agrees with the respective truncation of the exact evolution operator [feature (i)]. The remaining terms of the series endow the approximation with a physically reasonable functional form $\mathbf{F}(A)$ such that features (ii) and (iii) hold.

In Sec. II we first expand the exact evolution operator of the stochastically modulated quantum system in a power series in the perturbation operator $A$. For this purpose we make use of the superoperator formalism.[7] We then introduce the approximate (static ensemble) evolution operator and show its equality with the exact evolution operator up to third order in the perturbation. We discuss the properties of the approximation in the limit of very fast and very slow stochastic modulation. Finally, we investigate in how far the exact and the approximate evolution operator differ in their fourth order terms. We restrict our discussion in Sec. II to the case of a discrete stochastic process, but the approxima-

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tion developed holds also for a continuous stochastic process.

In Sec. III we apply the approximation to a physical system which has been investigated recently in experiment[8,9] and theory.[10,11] This system is similar to the ones investigated in Refs. 12–15 and involves two doublet (spin 1/2) molecules which are connected through short polymers $-(CH_2)_n-$, $n = 6,8,9,...,16$. The two doublets can exist in either a singlet or a triplet overall spin state. The experiment is capable to prepare through photoinduced electron transfer the doublet molecules in an initial singlet state. One can also monitor the subsequent overall spin state because reverse electron transfer according to the momentaneous spin state selects a product spin multiplicity (singlet or triplet) which can be identified spectroscopically. The dynamics of the doublet molecules, i.e., the dynamics of a pair of two electron spins, is governed by hyperfine interactions, which induce singlet–triplet transitions on a nanosecond time scale, and by Zeeman interaction with an external magnetic field. These two interactions are time independent and define the operator $A'$ above. A third interaction, the exchange interaction between the doublet molecules, which energetically separates singlet and triplet states, is time dependent and must be considered a random variable, defining the term $f(t)D'$ above. The likely reason for the random fluctuations of the exchange interaction is that this interaction depends on the distance between the doublet molecules and that this distance varies through the random folding motion of the polymer segment $-(CH_2)_n-$. It has been argued that the exchange interaction might also be mediated through the polymer (superexchange) in which case torsional motions around the polymer bonds lead to random fluctuations.[16]

The exchange interaction provides actually the dominant contribution to the spin Hamiltonian and, therefore, folding or torsional motion exerts a strong influence on the observed spin dynamics. This has been shown in Refs. 8–11. For the sake of demonstration we will study in this paper only a simple model of such spin dynamics in which the exchange interaction assumes six distinct values between which the system undergoes Markovian transitions. Our treatment does not rely on the mechanism of the exchange interaction, i.e., "through space", solvent-mediated "superexchange" or bridge-mediated superexchange.

## II. THEORY

### A. Preliminaries

The evolution of the quantum system of interest in the Hilbert space $\Omega$ spanned by the quantum states is governed by the stochastic Hamiltonian $H(t)$ defined in Eq. (1.1) and is described by the solution of the Liouville equation

$$\partial_t \rho = H^x(t)\rho, \tag{2.1}$$

where $\rho$ is the density operator. $H^x$ is the so-called superoperator[7] associated with the Hamiltonian $H$ and is defined through

$$H^x \rho = [H,\rho]. \tag{2.2}$$

$H^x$ is an operator which acts on elements of a space denoted by $\Omega^x$; the latter is the space spanned by the operators acting on elements of $\Omega$. (We will use in the following the phrase "$O$ is an operator acting in the space $S$" when $O$ acts on elements of $S$.) $H^x$ acts, e.g., on the density operator $\rho$. The matrix element of $H^x$ coupling the matrix elements $\rho_{ij}$ and $\rho_{kl}$ of the density operator has to be labeled by four indices and is

$$H^x_{ijkl} = H_{ik}\delta_{jl} - H_{lj}\delta_{ik}. \tag{2.3}$$

The time dependence of the Hamiltonian $H(t)$ is due to a random process of the scalar variable $f(t)$ with realizations $f_k$ from the set $\{f_1, f_2, ..., f_n\}$. To the stochastic states labeled by the index $k, k = 1,...,n$, correspond different realizations $H_k$ of the Hamiltonian

$$H_k = f_k D' + A'. \tag{2.4}$$

Random transitions between states $k$ and $l$ switch the Hamiltonian from $H_k$ to $H_l$. This stochastic process is described by the master equation (1.2) where $\mathbf{q}$ is an element of the probability space $\Sigma$ spanned by the realizations of the stochastic variable and where the master operator $\mathbf{l}$ acts in $\Sigma$.

It is well known that the time dependence of the Hamiltonian makes a solution of Eq. (2.1) cumbersome. A time-independent Liouville equation can be achieved[17] by extending the space in which Eq. (2.1) holds to the product space $\Omega^x \otimes \Sigma$ (as stated above, $\Omega^x$ is the space spanned by the quantum mechanical operators and $\Sigma$ is the space spanned by the stochastic states). The density matrix in this space is denoted by a vector $\boldsymbol{\rho}$ with $n$ elements $\rho_k, k = 1,...,n$, which are density matrices acting in the space $\Omega$ of quantum states. The index $k$ refers to stochastic states. $\boldsymbol{\rho}$ obeys the stochastic Liouville equation (SLE)

$$\partial_t \boldsymbol{\rho} = (-i\mathbf{H}^x + \mathbf{L})\boldsymbol{\rho}. \tag{2.5}$$

The operators acting in the space $\Omega^x \otimes \Sigma$ are denoted by uppercase, bold symbols. (Lowercase bold symbols, e.g., $\mathbf{l}$, denote operators acting in $\Sigma$, upper case symbols, e.g., $H_k$, denote operators acting in $\Omega$ and uppercase symbols with superscript $x$, e.g., $H^x$, denote operators acting in $\Omega^x$.) $\mathbf{H}^x$ is defined by the following block-diagonal matrix of superoperators associated with the Hamiltonians $H_k$

$$\mathbf{H}^x = \begin{pmatrix} H_1^x & & & \\ & H_2^x & & \\ & & \ddots & \\ & & & H_n^x \end{pmatrix}. \tag{2.6}$$

$\mathbf{L}$ is the Cartesian product of the identity superoperator $1^x$, acting in $\Omega^x$, and of $\mathbf{l}$, acting in $\Sigma$.

Equation (2.5) has the formal solution

$$\boldsymbol{\rho}[t] = \exp[(-i\mathbf{H}^x + \mathbf{L})t]\boldsymbol{\rho}_0, \tag{2.7}$$

where $\boldsymbol{\rho}_0 = \boldsymbol{\rho}[t=0]$. The discussion in the following will be in the Laplace domain since in this domain a power series expansion can be done more conveniently. Equation (2.7) reads after Laplace transformation

$$\boldsymbol{\rho}(s) = (s + i\mathbf{H}^x - \mathbf{L})^{-1}\boldsymbol{\rho}_0. \tag{2.8}$$

Here and in the following, we denote by curved brackets, e.g., $\boldsymbol{\rho}(s)$, operators in the Laplace domain, and by square brackets, e.g., $\boldsymbol{\rho}[t]$, operators in the time domain.[18] The ensemble-averaged density matrix $\rho(s)$ we seek is

$$\rho(s) = \langle \rho(s) \rangle = \sum_{k=1}^{n} \rho_k(s). \tag{2.9}$$

In case of identical quantum mechanical initial conditions in all stochastic states, i.e., in case there exists a single density matrix $\rho_0$ defined in $\Omega$ with $\rho_k[t=0] = \rho_0, k = 1,...,n$, and a population of the stochastic states according to their equilibrium probability, $\boldsymbol{\rho}_0$ can be written as the product $|0)\rho_0$, where $|0) = 1^x \otimes \mathbf{p}$ with $\mathbf{p}$ determined by Eq. (1.3). We also define the element $k$ with respect to the basis of the stochastic states in $\Sigma$: $|0)_k = 1^x p_k, k = 1,...,n$. The summation in Eq. (2.9) over all stochastic states can be expressed by $(0|\boldsymbol{\rho}(s)$, where $(0| = 1^x \otimes \mathbf{e}, \mathbf{e} = (1,1,...)$ denoting the left eigenvector of $\mathbf{l}$ to the eigenvalue zero. With these definitions the equation for the ensemble averaged density matrix $\rho(s)$ reads

$$\rho(s) = (0|[s + i\mathbf{H}^x - \mathbf{L}]^{-1}|0)\rho_0. \tag{2.10}$$

### B. Definition of the relevant propagator $U^x(s)$

For a substitution of the ensemble-averaged propagator $(0|[s + i\mathbf{H}^x - \mathbf{L}]^{-1}|0)$ in Eq. (2.10) by an approximate propagator we decompose the superoperator associated with the Hamiltonian into its diagonal and off-diagonal part. We choose the basis in a way that the stochastic part $f(t)D'$ of the Hamiltonian $H$ in Eq. (1.1) and the initial density matrix $\rho_0$ are simultaneously diagonal. This is possible since we required $[D', \rho_0] = 0$. The diagonal part $D^x$ is defined in terms of $D'^x$ and $A'^x$ by

$$D^x_{uvuv} = A'^x_{uvuv} + D'^x_{uvuv} f(t). \tag{2.11}$$

The off-diagonal part $A^x$ is not modulated stochastically and is the off-diagonal part of $A'^x$ in this basis

$$A^x_{uvu'v'} = A'^x_{uvu'v'}, \quad u \neq u' \vee v \neq v'. \tag{2.12}$$

$A^x$ induces transitions between the eigenstates of $D^x$ and is the perturbation operator. For a power series expansion of the propagator in the perturbation $A^x$ we write $H^x$ in the form

$$H^x = D^x + \lambda A^x. \tag{2.13}$$

The parameter $\lambda$ will be used to count the order in $A^x$ and will be set to one afterwards.

We are interested in the occupation probabilities of the quantum mechanical states and, thus, need only the diagonal part of the density matrix $\rho$. The operator $P^x$ projecting onto the relevant part of the density matrix $\rho$ is defined by[19] $P^x\rho = \mathrm{diag}(\rho_{11}, \rho_{22}, ..., \rho_{mm})$ where $m = \dim(\Omega)$ is the number of quantum states. For $P^x$ holds $P^xP^x = P^x$. For every superoperator $H^x$ associated to a Hamiltonian $H$ holds

$$P^xH^xP^x = 0, \tag{2.14}$$

and, in particular, for the diagonal part $D^x$,

$$P^xD^x = D^xP^x = 0. \tag{2.15}$$

Since $\rho_0$ is diagonal in our basis we have

$$P^x\rho_0 = \rho_0. \tag{2.16}$$

Hence the propagator of interest $U^x(s)$, which determines the relevant part $P^x\rho(s)$ of the density matrix, according to Eq. (2.10) is

$$U^x(s) = P^x(0|[s + i\mathbf{H}^x - \mathbf{L}]^{-1}|0)P^x. \tag{2.17}$$

### C. Expansion of $U^x(s)$

To evaluate Eq. (2.17) we write the resolvent in the form

$$[s + i\mathbf{H}^x - \mathbf{l}]^{-1} = [(s + i\mathbf{D}^x - \mathbf{L}) + i\lambda\,\mathbf{A}^x)]^{-1}, \tag{2.18}$$

where $\mathbf{D}^x$ and $\mathbf{A}^x$ are the extensions of $D^x$ and $A^x$, acting in $\Omega^x$, to the product space $\Omega^x \otimes \Sigma$. A formal expansion of Eq. (2.18) in a power series in $\lambda$ is

$$[s + i\mathbf{H}^x - \mathbf{L}]^{-1} = (s + i\mathbf{D}^x - \mathbf{L})^{-1} \times \sum_{n=0}^{\infty} [(-i\lambda\,\mathbf{A}^x)(s + i\mathbf{D}^x - \mathbf{L})^{-1}]^n. \tag{2.19}$$

In the following we also use $\mathbf{P}^x$, the extension of $P^x$ to $\Omega^x \otimes \Sigma$. To perform the projection and the ensemble average we make use of the relations

$$P^x(0| = (0|\mathbf{P}^x, \quad |0)P^x = \mathbf{P}^x|0), \tag{2.20}$$

$$\mathbf{P}^x(s + i\mathbf{D}^x - \mathbf{L})^{-1} = \mathbf{P}^x(s - \mathbf{L})^{-1},$$

$$(s + i\mathbf{D}^x - \mathbf{L})^{-1}\mathbf{P}^x = (s - \mathbf{L})^{-1}\mathbf{P}^x, \tag{2.21}$$

$$(0|(s - \mathbf{L})^{-1} = (0|s^{-1},$$

$$(s - \mathbf{L})^{-1}|0) = s^{-1}|0). \tag{2.22}$$

With Eq. (2.21) we obtain (note that the term linear in $\lambda$ does not contribute since $\mathbf{P}^x\mathbf{A}^x\mathbf{P}^x = 0$)

$$\mathbf{P}^x[s + i\mathbf{H}^x - \mathbf{L}]^{-1}\mathbf{P}^x = (s - \mathbf{L})^{-1}\mathbf{P}^x\{1 + \sum_{n=1}^{\infty} [(-i\lambda\,\mathbf{A}^x)(s + i\mathbf{D}^x - \mathbf{L})^{-1}]^n \times (-i\lambda\,\mathbf{A}^x)\mathbf{P}^x(s - \mathbf{L})^{-1}\} \tag{2.23}$$

and on account of Eqs. (2.17), (2.20), and (2.22),

$$U^x(s) = s^{-1}P^x\{1 + (0|\sum_{n=1}^{\infty} [(-i\lambda\,\mathbf{A}^x) \times (s + i\mathbf{D}^x - \mathbf{L})^{-1}]^n(-i\lambda\,\mathbf{A}^x)|0)P^xs^{-1}\}. \tag{2.24}$$

Explicitly stating the terms up to order $\lambda^3$ yields

$$U^x(s) = s^{-1}P^x - \lambda^2 s^{-2}P^x(0|\mathbf{A}^x[s + i\mathbf{D}^x - \mathbf{L}]^{-1}\mathbf{A}^x|0)P^x + i\lambda^3 s^{-2}P^x(0|\mathbf{A}^x(s + i\mathbf{D}^x - \mathbf{L})^{-1}\mathbf{A}^x(s + i\mathbf{D}^x - \mathbf{L})^{-1}\mathbf{A}^x|0)P^x + s^{-2}P^x(0|\sum_{n=3}^{\infty} (-i\lambda)^{n+1}[\mathbf{A}^x(s + i\mathbf{D}^x - \mathbf{L})^{-1}]^n\mathbf{A}^x|0)P^x. \tag{2.25}$$

The fact that the off-diagonal part $A^x$ is identical in all stochastic states implies

$$\mathbf{A}^x|0) = |0)A^x; \quad (0|\mathbf{A}^x = A^x(0| \tag{2.26}$$

and, therefore, we can rewrite Eq. (2.25) in the form

$$U^x(s) = s^{-1}P^x - \lambda^2 s^{-2}P^x A^x (0|[s + i\mathbf{D}^x - \mathbf{L}]^{-1}|0)A^x P^x + i\lambda^3 s^{-2} P^x A^x (0|(s + i\mathbf{D}^x - \mathbf{L})^{-1}\mathbf{A}^x (s + i\mathbf{D}^x - \mathbf{L})^{-1}|0)A^x P^x + O(\lambda^4). \tag{2.27}$$

In the following we evaluate the expansion (2.27) further and demonstrate in how far the assumption of only two distinct eigenvalues of $D'$ simplifies the propagator $U^x(s)$ up to order $\lambda^3$.

### D. Expressing the second order term of $U^x(s)$ through Kubo's line shape function

We examine the expression $\overline{D}^x(s) = (0|[s + i\mathbf{D}^x - \mathbf{L}]^{-1}|0)$ occuring in Eq. (2.27) with a prefactor $\lambda^2$. $\overline{D}^x(s)$ is a diagonal superoperator defined in $\Omega^x$. Since $\mathbf{L}$ is diagonal with respect to the elements of $\Omega^x$ the resolvent $[s + i\mathbf{D}^x - \mathbf{L}]^{-1}$ is represented by a block-diagonal matrix, with a block $[s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1}$ for every diagonal element $D^x_{uvuv}$ of $D^x$. The blocks describe operators acting in $\Sigma$. The matrix $\mathbf{d}_{uv}$ is diagonal in $\Sigma$ and defined by

$$\mathbf{d}_{uv,kl} = \mathbf{D}^x_{uvuv,kl} = (A'^x_{uvuv} + D'^x_{uvuv} f_k)\delta_{kl}. \tag{2.28}$$

The indices $u,v$ refer to quantum states in $\Omega$, the indices $k,l$ refer to stochastic states in $\Sigma$. The decomposition of $[s + i\mathbf{D}^x - \mathbf{L}]^{-1}$ into the above block-diagonal matrix implies that each diagonal element $uvuv$ of $\overline{D}^x(s)$ can be expressed by

$$\overline{D}^x_{uvuv}(s) = {}_{uv}(0|[s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1}|0)_{uv}, \tag{2.29}$$

where $|0)_{uv,k} = p_k 1^x_{uvuv} = p_k$, and ${}_{uv,k}(0| = 1^x_{uvuv} = 1$. In the following we will suppress the index $uv$ of ${}_{uv}(0|$ and of $|0)_{uv}$ since the reduction to a particular element $uv$ is obvious from the appearance of $\mathbf{d}_{uv}$.

The expression $(0|[s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1}|0)$ can be written by means of Kubo's line shape function of an oscillator with random frequency modulation[20]

$$(0|[s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1}|0) = \int_{-\infty}^{\infty} d\omega\, I_{uv}(\omega)(s + i\omega)^{-1} \tag{2.30}$$

with the line shape function $I_{uv}(\omega)$ given by

$$I_{uv}(\omega) = \frac{1}{\pi}\mathrm{Re}(0|[i\,\mathbf{d}_{uv} - \omega) - \mathbf{l}]^{-1}|0). \tag{2.31}$$

The approximation suggested in this paper tests on the fact that the stochastic quantum system considered ($D'$ having only two distinct eigenvalues) can actually be described by a single distribution rather than a set of distributions [one distribution $I_{uv}(\omega)$ for each element of $D^x$], as Eqs. (2.30) and (2.31) seem to suggest. To show this we denote the two different eigenvalues of $D'$ by $D'_1, D'_2$. Since $D'$ is diagonal in our basis, a particular element $D'_{uu}$ can assume the value $D'_1$ or $D'_2$. With this definition the elements of $\mathbf{d}_{uv}$ read

$$\mathbf{d}_{uv,kk} = A'^x_{uvuv} + (D'_{uu} - D'_{vv})f_k = A'^x_{uvuv} + \Delta_{uv}(D'_1 - D'_2)f_k, \tag{2.32}$$

where $\Delta_{uv}$ assumes one of the three values $-1, 0$, or $1$, since the difference $(D'_{uu} - D'_{vv})$ can be $-(D'_1 - D'_2)$, 0, or $(D'_1 - D'_2)$. We can assume $(D'_1 - D'_2) = 1$ since this term can be absorbed by a transformation of the stochastic variable $f(t) \to \tilde{f}(t) = f(t)(D'_1 - D'_2)$. The constant part $A'^x_{uvuv}$ of $\mathbf{d}_{uv}$ can be separated from the distribution $I_{uv}(\omega)$ by shift of the variable.

For $\Delta_{uv} = \pm 1$ we obtain, after a variable transformation $\omega = j\Delta_{uv} + A'^x_{uvuv}$,

$$\overline{D}^x_{uvuv}(s) = \int_{-\infty}^{\infty} dj I(j)[s + i(A'^x_{uvuv} + j\Delta_{uv})]^{-1} = \int_{-\infty}^{\infty} dj I(j)[s + id_{uv}(j)]^{-1} \tag{2.33}$$

with

$$I(j) = \frac{1}{\pi}\mathrm{Re}(0|[i(\mathbf{f} - j) - \mathbf{l}]^{-1}|0), \tag{2.34}$$

where $d_{uv}(j) = A'^x_{uvuv} + j\Delta_{uv}$. $\mathbf{f}$ is the matrix $\mathbf{f} = \mathrm{diag}(f_1 f_2, \ldots f_n)$ and acts in $\Sigma$. For $\Delta_{uv} = 0$ follows from Eqs. (2.28) and (2.29) $\overline{D}^x_{uvuv}(s) = [s + iA'^x_{uvuv}]^{-1}$. Equation (2.33) holds also in this case, since the distribution $I(j)$ as defined in Eq. (2.33) is normalized,

$$\int_{-\infty}^{\infty} dj I(j) = 1. \tag{2.35}$$

Hence, with the definition

$$D^x_{uvuv}(j) = A'^x_{uvuv} + j\Delta_{uv} \tag{2.36}$$

we obtain for $\overline{D}^x(s)$,

$$(0|[s + i\mathbf{D}^x - \mathbf{L}]^{-1}|0) = \int_{-\infty}^{\infty} dj I(j)[s + iD^x(j)]^{-1}. \tag{2.37}$$

### E. Expressing the third order term of $U^x(s)$ through Kubo's line shape function

Next we examine the operator $\overline{A}^x(s) = (0|[s + i\mathbf{D}^x - \mathbf{L}]^{-1}\mathbf{A}^x[s + i\mathbf{D}^x - \mathbf{L}]^{-1}|0)$ which acts in $\Omega^x$ and occurs with a prefactor $\lambda^3$ in Eq. (2.27). Since for the superoperator $A^x$ in $\Omega^x$ holds $A_{uvu'v'} = 0$ for $u \neq u' \wedge v \neq v'$, the number of possible combinations of indices for nonvanishing elements of $\overline{A}^x(s)$ is limited to two: (i) $\overline{A}^x_{uvuv'}(s)$ and (ii) $\overline{A}^x_{uvu'v}(s)$. As before we make use of the

fact that the matrix $[s+i\mathbf{D}^x-\mathbf{L}]^{-1}$ is represented by a block-diagonal matrix with blocks $[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}$, where we define $\mathbf{d}_{uv}=A'^x_{uvuv}+\mathbf{f}\Delta_{uv}$. This and the fact, that $\mathbf{A}^x$ reduced to the space $\Sigma$ is the identity operator acting in $\Sigma$ implies that the nonvanishing elements of $\overline{A}^x(s)$ can be represented by

(i) $(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)A^x_{uvuv'}$,

(ii) $(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{u'v}-\mathbf{1}]^{-1}|0)A^x_{uvu'v}$.

We will discuss only the term (i) since equivalent arguments hold for (ii). From the definition of $\Delta_{uv}$ in Eq. (2.32) follows that neither $\Delta_{uv'}$ nor $\Delta_{u'v}$ can have a sign different from $\Delta_{uv}$. One can conclude that expressions with different signs of $\Delta$ do not occur in $\overline{A}^x(s)$. In the following we use again the definition $d_{uv}(j)=A'^x_{uvuv}+j\Delta_{uv}$. In the case $\Delta_{uv'}=\Delta_{uv'}=0$ Eq. (2.35) implies

$$(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)=\int_{-\infty}^{\infty}djI(j)[s+id_{uv}(j)]^{-1}[s+id_{uv'}(j)]^{-1}. \tag{2.38}$$

In the case $\Delta_{uv}\neq 0\wedge\Delta_{uv'}=0$ one can simplify

$$(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)=(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}|0)[s+iA'^x_{uv'uv'}]^{-1},$$

that is,

$$(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)=\int_{-\infty}^{\infty}djI(j)[s+id_{uv}(j)]^{-1}[s+id_{uv'}(j)]^{-1}. \tag{2.39}$$

Equation (2.39) holds obviously also in the case $\Delta_{uv}=0\wedge\Delta_{uv'}\neq 0$. To study the case $\Delta_{uv}=\Delta_{uv'}\neq 0$ we investigate the back transformation of $g(s)=(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)$ into the time domain. By means of the convolution theorem one finds

$$g[t]=\int_0^t dt'\,(0|\exp[(-i\mathbf{d}_{uv}+\mathbf{1})(t-t')]\times[(-i\mathbf{d}_{uv'}-\mathbf{1})t']|0)$$

from which follows by means of $\mathbf{d}_{uv'}-\mathbf{d}_{uv}=A'^x_{uv'uv'}-A'^x_{uvuv}$,

$$g[t]=(0|\exp[(-i\mathbf{d}_{uv}+\mathbf{1})t]|0)\int_0^t dt'\times\exp[-i(A'^x_{uv'uv'}-A'^x_{uvuv})t']. \tag{2.40}$$

Equations (2.29) and (2.33) in the time domain yield

$$g[t]=\int_{-\infty}^{\infty}dj\,I(j)\exp[-id_{uv}(j)t]\int_0^t dt'\times\exp[-i(A'^x_{uv'uv'}-A'^x_{uvuv})t']$$

from which follows by means of $A'^x_{uv'uv'}-A'^x_{uvuv}=d_{uv'}(j)-d_{uv}(j)$,

$$g[t]=\int_{-\infty}^{\infty}dj\,I(j)\int_0^t dt'\times\exp[-id_{uv}(j)(t-t')]\exp[-id_{uv'}(j)t']. \tag{2.41}$$

In the Laplace domain this reads

$$(0|[s+i\mathbf{d}_{uv}-\mathbf{1}]^{-1}[s+i\mathbf{d}_{uv'}-\mathbf{1}]^{-1}|0)=\int_{-\infty}^{\infty}dj\,I(j)[s+id_{uv}(j)]^{-1}[s+id_{uv'}(j)]^{-1}. \tag{2.42}$$

Thus, on account of Eqs. (2.38), (2.39) and (2.42) all possible matrix elements of $\overline{A}^x(s)$ can be expressed in the form

$$(0|[s+i\mathbf{D}^x-\mathbf{L}]^{-1}\mathbf{A}^x[s+i\mathbf{D}^x-\mathbf{L}]^{-1}|0)=\int_{-\infty}^{\infty}djI(j)[s+iD^x(j)]^{-1}A^x[s+iD^x(j)]^{-1}. \tag{2.43}$$

Equations (2.37) and (2.43) allow us to represent finally $U^x(s)$ up to order $\lambda^3$ by means of a single distribution $I(j)$,

$$U^x(s)=P^x(0|[s+i\mathbf{H}^x-\mathbf{L}]^{-1}|0)P^x=s^{-1}P^x-\lambda^2s^{-2}P^xA^x\int_{-\infty}^{\infty}djI(j)[s+iD^x(j)]^{-1}A^xP^x+i\lambda^3s^{-2}P^xA^x\int_{-\infty}^{\infty}dj\,I(j)[s+iD^x(j)]^{-1}A^x[s+iD^x(j)]^{-1}A^xP^x+O(\lambda^4). \tag{2.44}$$

### F. Definition of approximate propagator $\tilde{U}^x(s)$ and proof of agreement with $U^x(s)$ up to third order

We want to demonstrate now that the exact evolution operator (2.17) can be approximated by an evolution operator $\tilde{U}^x(s)$ which is an ensemble average of propagators corresponding to time-independent Hamiltonians $H(j)=jD'+A'$, namely

$$\tilde{U}^x(s)=\int_{-\infty}^{\infty}dj\,I(j)P^x[s+iH^x(j)]^{-1}P^x. \tag{2.45}$$

With the definitions (2.11), (2.12) and (2.36) for $D^x(j)$ and $A^x$ the approximation $\tilde{U}^x(s)$ can be written

$$\tilde{U}^x(s)=P^x\int_{-\infty}^{\infty}dj\,I(j)\{s+i[D^x(j)+A^x]\}^{-1}P^x. \tag{2.46}$$

To show that $\tilde{U}^x(s)$ is identical with the exact propagator $U^x(s)$ up to third order in $A^x$ we insert in Eq. (2.46) like in Eq. (2.13) the parameter $\lambda$, and expand $\tilde{U}^x(s)$ in a power series in $\lambda A^x$. Applying the expansion (2.19) to Eq. (2.46) we obtain

$$\begin{aligned}\tilde{U}^x(s) &= P^x \int_{-\infty}^{\infty} dj\, I(j)\{s + i[D^x(j) + \lambda A^x]\}^{-1} P^x \\ &= P^x \int_{-\infty}^{\infty} dj\, I(j)[s + iD^x(j)]^{-1} \sum_{n=0}^{\infty} \{(-i\lambda A^x)[s + iD^x(j)]^{-1}\}^n P^x \\ &= s^{-1}P^x - \lambda^2 s^{-2} P^x A^x \int_{-\infty}^{\infty} dj\, I(j)[s + iD^x(j)]^{-1} A^x P^x \\ &\quad + i\lambda^3 s^{-2} P^x A^x \int_{-\infty}^{\infty} dj\, I(j)[s + iD^x(j)]^{-1} A^x [s + iD^x(j)]^{-1} A^x P^x \\ &\quad + s^{-2} \int_{-\infty}^{\infty} dj\, I(j) \sum_{n=3}^{\infty} (-i\lambda)^{n+1} P^x [A^x [s + iD^x(j)]^{-1}]^n A^x P^x. \end{aligned} \tag{2.47}$$

Comparing this expansion with the expansion of $U^x(s)$ as given by Eq. (2.44) shows that $U^x(s)$ and $\tilde{U}^x(s)$ are identical up to third order in $A^x$. This implies that $\tilde{U}^x$ is a short-time approximation, the time scale being defined by the off-diagonal elements of $A'$ in Eq. (1.1).

The approximation $\tilde{U}^x(s)$ as given by Eq. (2.46) can be extended to a continuous stochastic process $f(t)$ in which case the discrete stochastic operators $\mathbf{l}$,$\mathbf{L}$ are replaced by differential operators $l(f)$,$L(f)$. The vector $\boldsymbol{\rho}$ of density matrices is replaced by a distribution $\rho(f)$, e.g., $\rho_0 = |0)\rho_0 \rightarrow 1^x p(f)\rho_0$, and the sum over all stochastic states by $(0|\boldsymbol{\rho}$ is replaced by an integral $\int_{f_1}^{f_2} df\, \rho(f)$.

### G. $\tilde{U}^x$ converges to $U^x$ in case of fast and slow stochastic modulation of $H(t)$

In case of extremely fast stochastic modulation the spectrum $I(j)$ of the stochastically modulated parameter $f(t)$ approaches a delta function[6,21] at the mean value $\langle f\rangle = \sum_{k=1}^{n} p_k f_k$ of $f(t)$, i.e., $I(j) \rightarrow \delta(j - \langle f\rangle)$. In this so-called motional narrowing limit the approximation (2.46) yields

$$\begin{aligned}\tilde{U}^x(s) &= P^x\{s + i[D^x(\langle f\rangle) + A^x]^{-1} P^x \\ &= P^x[s + i(\langle f\rangle D'^x + A'^x)]^{-1} P^x \\ &= P^x[s + i\langle H^x\rangle]^{-1} P^x, \end{aligned} \tag{2.48}$$

where $\langle H^x\rangle = \sum_{n}^{k=1} p_k H_k^x = \langle f\rangle D'^x + A'^x$ is the superoperator corresponding to the average Hamiltonian. Equation (2.48) according to Ref. 22 is also the asymptotic form of $U^x(s)$.

For vanishing stochastic motion as shown by Kubo[6,21] $I(j)$ is the equilibrium distribution of $f(t)$ defined by Eq. (1.3), i.e., $I(j) = \sum_{i=1}^{n} p_k \delta(j - f_k)$. Hence, $\tilde{U}^x(s)$ is in this limit

$$\tilde{U}^x(s) = \sum_{k=1}^{n} p_k U_k^x(s), \tag{2.49}$$

where $U_k^x(s) = P^x[s + iH_k^x]^{-1} P^x$. According to Ref. 22 the exact propagator $U^x(s)$ in this limit is also given by Eq. (2.49).

### H. $U^x$ conserves the trace of the density matrix

The evolution operator $\tilde{U}^x$ defined by Eq. (2.45) reads in the time domain

$$\tilde{U}^x[t] = \int_{-\infty}^{\infty} dj\, I(j) P^x \exp[-iH^x(j)t] P^x. \tag{2.50}$$

This is the time evolution operator for the relevant part $P^x\tilde{\rho}[t]P^x$ of a density matrix $\tilde{\rho}[t]$ obeying the Liouville equation

$$\partial_t \tilde{\rho}[t] = -i \int_{-\infty}^{\infty} dj\, I(j) H^x(j) \tilde{\rho}[t]. \tag{2.51}$$

From Eqs. (2.2), (2.35), and (2.51) one can conclude that the approximation $U^x[t]$ conserves the trace of the density matrix, i.e., $\mathrm{tr}\,\tilde{\rho}[t] = \mathrm{tr}\,\tilde{\rho}[t=0]$. Hence, with $\tilde{\rho}[0] = \rho[0]$ the approximation $\tilde{U}^x[t]$ reproduces the trace of the exact density matrix at all times.

### I. Illustration in how far $\tilde{U}^x(s)$ and $U^x(s)$ deviate in fourth order

To illustrate in how far the approximation $\tilde{U}^x(s)$ deviates in order $\lambda^4$ from the exact solution $U^x(s)$ we consider a special form of the stochastic operator $\mathbf{l}$. The $\mathbf{l}$ considered describes what is called the Kubo–Anderson process (KAP),[23] the strong collision approximation,[24] or equivalently, the random phase approximation.[22] This process, a particular realization of a stationary, Markovian, and ergodic random process, is characterized by a time scale $\tau$ and assumes that for any stochastic state $|k)$ with $(0|k) = 1$ holds

$$\mathbf{l}|k) = \tau^{-1}[|0) - |k)]. \tag{2.52}$$

This leads to

$$\begin{aligned}&\exp(\mathbf{l}t)|k) = |0) + \exp(-\tau^{-1}t)[|k) - |0)], \\ &[s - \mathbf{l}]^{-1}|k) = s^{-1}|0) + [s + \tau^{-1}]^{-1}[|k) - |0)]. \end{aligned} \tag{2.53}$$

For the intended illustration it suffices to consider only a particular contribution to the fourth order term in Eq. (2.25):

$$\begin{aligned}&(0|[s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1} A^x_{uvu'v'} [s + i\mathbf{d}_{uv'} - \mathbf{l}]^{-1} \\ &\quad \times A^x_{uv'uv} [s + i\mathbf{d}_{uv} - \mathbf{l}]^{-1} |0). \end{aligned} \tag{2.54}$$

We will further assume $\Delta_{uv'}=0$. Inserting the identity $\Sigma_{k=1}^{n}|k)(k|$ and suppressing the constants $A^{x}_{uvuv'}, A^{x}_{uv'uv}$ one can write

$$\begin{aligned}
&\sum_{k=1}^{n}(0|[s+i\mathbf{d}_{uv}-1]^{-1}[s+i\mathbf{d}_{uv'}-1]^{-1}|k)(k|[s+i\mathbf{d}_{uv}-1]^{-1}|0)\\
&\quad=\sum_{k=1}^{n}(0|[s+i\mathbf{d}_{uv}-1]^{-1}\{[s+iA^{\prime x}_{uv'uv'}]^{-1}|0)+[s+iA^{\prime x}_{uv'uv'}+\tau^{-1}]^{-1}[|k)-|0)]\}(k|[s+i\mathbf{d}_{uv}-1]^{-1}|0)\\
&\quad=(0|[s+i\mathbf{d}_{uv}-1]^{-1}|0)\{[s+iA^{\prime x}_{uv'uv'}]^{-1}-[s+iA^{\prime x}_{uv'uv'}+\tau^{-1}]^{-1}\}(0|[s+i\mathbf{d}_{uv}-1]^{-1}|0)\\
&\qquad+(0|[s+i\mathbf{d}_{uv}-1]^{-1}[s+iA^{\prime x}_{uv'uv'}+\tau^{-1}]^{-1}[s+i\mathbf{d}_{uv}-1]^{-1}|0)\\
&\quad=\int_{-\infty}^{\infty}dj_1\,I(j_1)\int_{-\infty}^{\infty}dj_2\,I(j_2)[s+id_{uv}(j_1)]^{-1}[s+id_{uv}(j_2)]^{-1}\{[s+iA^{\prime x}_{uv'uv'}{}^{-1}]-[s+iA^{\prime x}_{uv'uv'}+\tau^{-1}]^{-1}\}\\
&\qquad+\int_{-\infty}^{\infty}dj\,I(j)[s+id_{uv}(j)]^{-1}[s+iA^{\prime x}_{uv'uv'}+\tau^{-1}]^{-1}[s+id_{uv}(j)]^{-1}. \qquad (2.55)
\end{aligned}$$

The corresponding term in expansion (2.47) of $\tilde{U}^{x}$ reads

$$\int_{-\infty}^{\infty}dj\,I(j)[s+id_{uv}(j)]^{-1}[s+iA^{\prime x}_{uv'uv'}]^{-1}\times[s+id_{uv}(j)]^{-1}. \qquad (2.56)$$

Comparing Eqs. (2.55) and (2.56) one finds that the approximation $\tilde{U}^{x}(s)$ does not include the double integral over $j_1$ and $j_2$ in Eq. (2.55). This double integral arises from jumps between stochastic states while $\Delta_{uv'}=0$. The integral (2.56) contains only paths with the same stochastic state $|k)$ at the begin and end of $\Delta_{uv'}=0$. The expressions (2.55) and (2.56) differ further in the single integral over $j$. While in Eq. (2.55) the integrand explicitly depends on the time scale $\tau$ of the stochastic process, in Eq. (2.56) the integrand depends on $\tau$ only implicitly through $I(j)$.

## III. APPLICATION

In this chapter we demonstrate the application of the approximation $\tilde{U}^{x}(s)$ to the case of a pair of doublet molecules with a stochastic modulation of exchange interactions involving six different realizations.[25] The spin dynamics of this system is governed by the Hamiltonian $H$ (see Refs. 26 and 27),

$$\begin{aligned}
&H(t)=H_1+H_2+J(t)(Q_T-Q_S),\\
&H_i=a_i\mathbf{I}_i\cdot\mathbf{S}_i+\mathbf{B}\cdot\mathbf{S}_i,\quad i=1,2,\\
&J(t)\in\{J_k;k=1,\ldots,6\},\\
&Q_T=\tfrac{3}{4}+\mathbf{S}_1\cdot\mathbf{S}_2,\quad Q_S=\tfrac{1}{4}-\mathbf{S}_1\cdot\mathbf{S}_2.
\end{aligned} \qquad (3.1)$$

$H_i$ describes the hyperfine interaction of the electron spin $\mathbf{S}_i$ on molecule $i$ with a single nuclear spin 1/2 described by $\mathbf{I}_i$ and with the magnetic field $\mathbf{B}$ (Zeeman interaction). We assume that on each molecule only a single nuclear spin interacts with the electron spin. The constants $a_i$ account for the strength of the hyperfine coupling between $\mathbf{S}_i$ and $\mathbf{I}_i$. We assume values $a_1=11$ G and $a_2=37$ G. The term $J(t)(Q_T-Q_S)$ describes the randomly modulated exchange interaction. $Q_S$ and $Q_T$ are the projections onto the electronic singlet and triplet states. $D'$ defined in Eq. (1.1) is in this case $D'=Q_T-Q_S$. The time-independent operators $H_1$ and $H_2$ in the Hamiltonian yield the operator $A'$ of Eq. (1.1), i.e., $A'=H_1+H_2$. The Zeeman part of $H_i$ is diagonal in the same basis as the projectors $Q_T$ and $Q_S$ and, thus, contributes to the diagonal operator $D$ defined in Sec. II. The hyperfine part of $H_i$ contributes to the off-diagonal operator $A$ and induces transitions between singlet and triplet states. The observable which we consider for the system governed by Eq. (3.1) is the magnetic field-dependent triplet yield[28] $\Phi_T(B)=\mathrm{tr}[sQ_TU^{x}(s)\rho_0]$ where $s$ is determine by the lifetime $\tau_0$ of the doublet pair, i.e., $s=\tau_0^{-1}$.

Our approximation can be applied to this system, since the doublet pair is prepared in a pure singlet state, i.e., the initial density matrix $\rho_0=Q_S/\mathrm{tr}(Q_S)$ commutes with the stochastically time-dependent part of the Hamiltonian $J(t)(Q_T-Q_S)$, and since $D'=Q_T-Q_S$ has only two eigenvalues, namely $+1$ for triplet states and $-1$ for singlet states.

The randomly modulated exchange interaction in our model system leads to a time-dependent (fluctuating) energy separation $2J(t)$ between the triplet states and the singlet state. The approximation derived in Sec. II represents this fluctuating separation by a static distribution $I(j)$ of separations $2j$. Application of Eq. (2.34) to the present case yields

$$\begin{aligned}
&I(j)=\frac{2}{\pi}\mathrm{Re}(0|[2i(\mathbf{J}-j)-1]^{-1}|0),\\
&\mathbf{J}=\mathrm{diag}(J_1,J_2,\ldots,J_6).
\end{aligned} \qquad (3.2)$$

The function $I(j)$ can be interpreted as the "spectrum of exchange interactions" which the electron spins experience due to random jumps between the six possible values $J_k$. $I(j)$ depends on the transition operator $\mathbf{l}$ and, hence, on the stochastic dynamics of $J(t)$. This dependence will be discussed now.

We assume that the stochastic jumps between the realizations of the exchange interaction $J_k$ take place only between nearest neighbors $J_k, J_{k\pm1}$ (birth–death process). Assuming equal equilibrium probabilities of the states corresponding to each $J_k$ the stochastic operator $\mathbf{l}$ has the form (only nonvanishing matrix elements are presented)

$$\mathbf{l}=\tau^{-1}\begin{pmatrix} -1 & 1 & & & & \\ 1 & -2 & 1 & & & \\ & \cdot & \cdot & \cdot & & \\ & & 1 & -2 & 1 & \\ & & & 1 & -1 \end{pmatrix}, \tag{3.3}$$

where $\tau$ denotes the mean time interval between two successive jumps. To obtain the spectrum $I(j)$ one first solves the tridiagonal linear system

$$[2i(\mathbf{J}-j)-\mathbf{l}]|x)=|0)$$

and evaluates $I(j)=(2/\pi)\mathrm{Re}(0|x)$, where $|0)$ and $(0|$ are defined as in Sec. II D.

Figure 1 shows the spectrum of exchange interactions $I(j)$ for $J_k=0$, 60, 120, 180, 240, and 300 G and for $\tau=10^2$ ns [Fig. 1(a)], for $\tau=1$ ns [Fig. 1(b)], and for $\tau=10^{-2}$ ns [Fig. 1(c)]. The shape of the spectrum $I(j)$ depends sensitively on the ratio of the jump frequency $\tau^{-1}$ to the frequency differences implied by $J_k-J_{k\pm1}$. The difference between the exchange interactions $J_k$ is $\Delta J=60$ G. This corresponds to a frequency difference of about 2 $\mathrm{ns}^{-1}$. For slow jumps characterized by $\tau=10^2$ ns the ratio $\tau^{-1}/\Delta J$ is very small. In this case $I(j)$ shows peaks centered at the values $J_k$ [see Fig. 1(a)]. An intermediate jump rate $\tau=1$ ns leads to a spectrum $I(j)$ smeared out over the whole range of possible $J_k$ values [see Fig. 1(b)]. For fast jumps characterized by $\tau=10^{-2}$ ns the ratio $\tau^{-1}/\Delta J$ is very large and $I(j)$ peaks at the average $J$ value $\langle J\rangle=(1/6)\Sigma_{k=1}^{6}J_k$ [see Fig. 1(c)]. The rate $\tau=10^{-2}$ ns is not large enough yet to make $I(j)$ collapse to a $\delta$ function as described in Sec. II G for the motional narrowing limit.

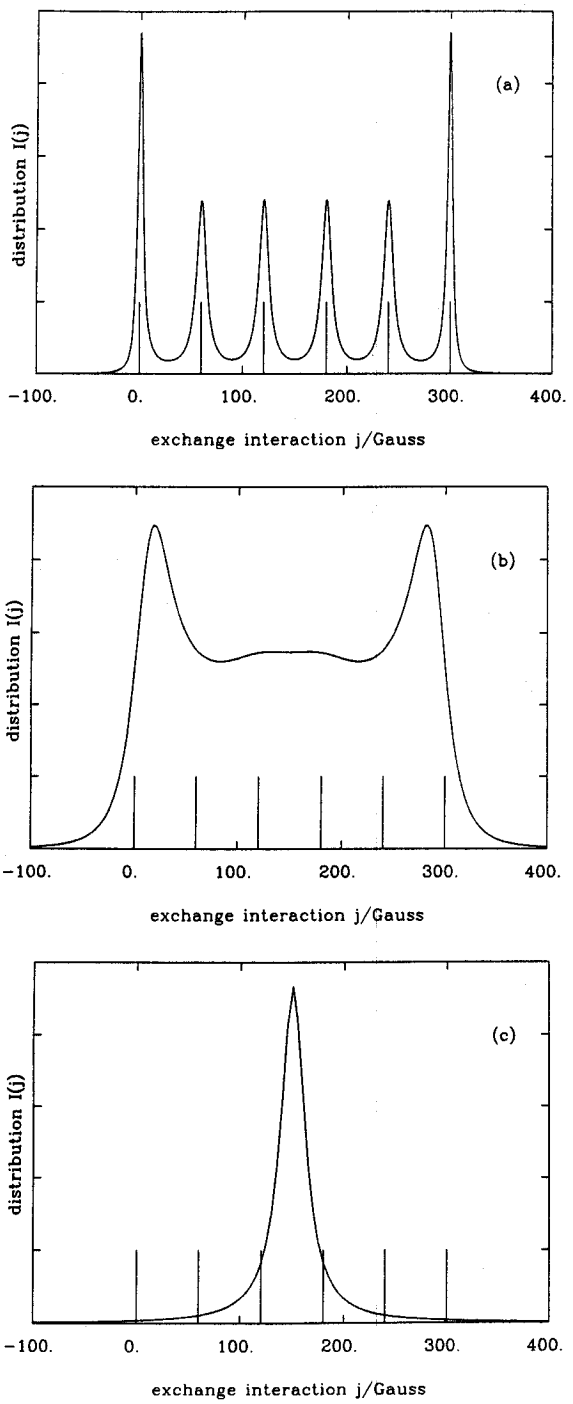


FIG. 1. Distribution of singlet–triplet energy differences $2j$ as given by the function $I(j)$ of Eq. (3.2). The system can exist in six different states $k$ to which correspond six different exchange interactions $J_k$: 0, 60, 120, 180, 240, and 300 G. Three different first order transfer rate constants $\tau^{-1}$ had been assumed: (a) $10^{-2}$ $\mathrm{ns}^{-1}$; (b) 1 $\mathrm{ns}^{-1}$; (c) $10^{-2}$ $\mathrm{ns}^{-1}$.

To demonstrate the accuracy of the approximation $\tilde{U}^x$, based on the distribution of exchange interactions $I(j)$ given by Eq. (3.2), we compare the exact triplet yield $\Phi_T(B)$ with the approximation $\tilde{\Phi}_T(B)=\mathrm{tr}[\tau_0^{-1}Q_T\tilde{U}^x(\tau_0^{-1})\rho_0]$. The approximation $\tilde{U}^x$ implies that the quantum system with stochastically modulated Hamiltonian $H(t)$ evolves like an ensemble of quantum systems with time-independent Hamiltonians $H(j)=H_1+H_2+j(Q_T-Q_S)$ when the exchange interaction $j$ is distributed according to $I(j)$. The approximation holds only to third order in $A^x\tau_0$. This follows from

$$U^x(\tau_0^{-1})=\tau_0P^x(0|[1+i\tau_0(\mathbf{D}^x+\mathbf{A}^x)-\tau_0\mathbf{L}]^{-1}|0)P^x.$$

The time scale associated with $A^x$ for the example considered is given by the hyperfine coupling constants $a_i$ and is $\bar{a}^{-1}\approx1.5$ ns, i.e., the approximation holds to order $(\tau_0/1.5\ \mathrm{ns})^3$. In Figs. 2 and 3 we compare $\Phi_T(B)$ and $\tilde{\Phi}_T(B)$ for lifetimes $\tau_0$ smaller and larger than 1.5 ns, respectively.

For a short lifetime $\tau_0=1$ ns, i.e., $\tau_0\bar{a}\approx2/3$, the approximation agrees well with the exact solution as shown in Fig. 2. The exact solution denoted by $\times$ in Fig. 2, obtained by

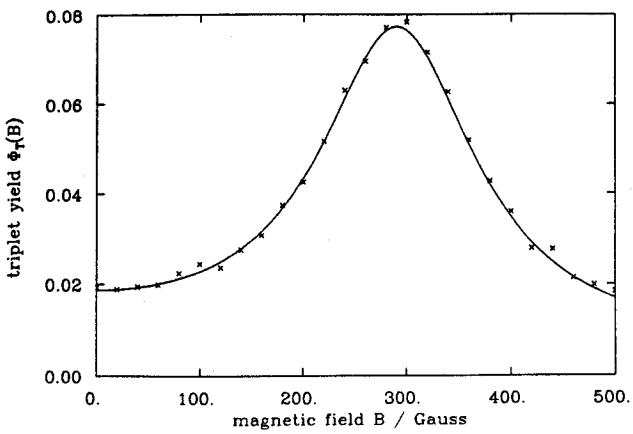


FIG. 2. Magnetic field dependence of the triplet yield $\Phi_T(B)$ for the stochastic quantum system of Fig. 1(c) evaluated by simulation ($\times\times\times$) and evaluated by the approximation (2.45) (—). The assumed lifetime $\tau_0$ is 1 ns.

Monte Carlo integration,[10] shows the characteristic fluctuations of the Monte Carlo method. For a long lifetime $\tau_0 = 10$ ns, i.e., $\tau_0 \bar{a} \approx 7$, the case shown in Fig. 3, one observes a systematic deviation between approximation and exact solution.

However, the approximation agrees qualitatively with the exact solution. The triplet yield $\tilde{\Phi}_T(B)$ as well as $\Phi_T(B)$ exhibit a maximum at the magnetic field $B_{\max} \approx 300$ G, i.e., at a field for which the singlet state and the triplet state $T_{-1}$ are degenerate in the case of the most probable exchange interaction $J_{\max} = 150$ G in the static ensemble. Further agreement between $\tilde{\Phi}_T(B)$ and $\Phi_T(B)$ can be demonstrated by inspecting other characteristics of the magnetic field dependence of the triplet yield. The first characteristic considered is the ratio $R = \Phi_T(B_{\max})/\Phi_T(0)$, the second characteristic is the width $B_h$, defined by $\Phi_T(B_{\max} - B_h) = [\Phi_T(B_{\max}) + \Phi_T(0)]/2$. In Fig. 3 the ratio $\Phi_T(B_{\max})/\Phi(0)$ is about 7, whereas $\Phi_T(B_{\max})/\tilde{\Phi}_T(0)$ is about 10. $B_h$ for $\Phi_T$ as well as $\tilde{\Phi}_T$ is about 70 G. This implies that the qualitative magnetic field dependence of the triplet yield is described well by means of the spectrum $I(j)$ of exchange interactions even in the case of a long lifetime of the doublet pair.

In Ref. 11 the authors have shown that the magnetic field dependence of the triplet yield as observed in Refs. 8 and 9 for doublet pairs linked by aliphatic chains $-(CH_2)_n-$ with $n = 8,9,10$ can be explained by an analysis of the spectrum $I(j)$ of exchange interactions. Since the lifetime $\tau_0$ of the doublet pairs investigated in Refs. 8 and 9 is, according to Ref. 9, greater than 10 ns, the static ensemble approximation does not give quantitatively correct results. However, comparing the triplet yield, obtained for this system by a numerical solution of the SLE (2.8), with the spectrum of the exchange interaction $I(j)$, the authors showed in Ref. 11 that the magnetic field dependence of the triplet yield can be described well, as in the example given above, by means of the spectrum $I(j)$. It has been found that the magnetic field $B_{\max}$ at which the triplet yield assumes a maximum and the exchange interaction $J_{\max}$ with highest probability $I(j)$ are related by $B_{\max} \approx 2J_{\max}$. The values $R$ and $B_h$ for $\Phi_T$, defined above, show the same dependence on the length $n$ of the aliphatic chain $-(CH_2)_n-$ as the corresponding quantities for the spectrum $I(j)$, e.g., $R_I = I(J_{\max})/I(0)$. This implies that the spectrum of exchange interactions $I(j)$ qualitatively describes the magnetic field dependence of the triplet yield and, thus, the physically interesting dynamics of this stochastic quantum system.

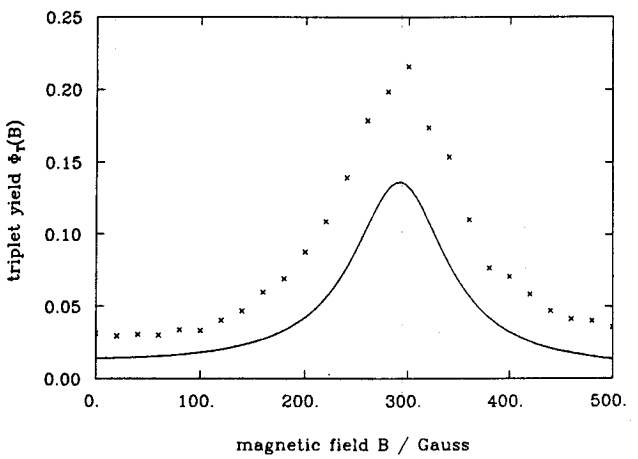


FIG. 3. Demonstration of the error connected with the approximation (2.45): The diagram shows the magnetic field dependence of the triplet yield $\Phi_T(B)$ as evaluated by a simulation ($\times\times\times$) and by the approximation (—) for a long lifetime, i.e., $\tau_0 = 10$ ns.

## IV. SUMMARY

In this paper we have introduced a static ensemble approximation for a stochastically modulated quantum system. The stochastically modulated part of the Hamiltonian is assumed to be represented by the product of a randomly modulated scalar function and a quantum mechanical operator with only two distinct eigenvalues. A time-independent perturbation induces transitions between the initially occupied eigenstates of the randomly modulated part of the Hamiltonian. The suggested approximation replaces the randomly modulated Hamiltonian of the system by a distribution of time-independent Hamiltonians. The distribution of the time-independent Hamiltonians has been derived. We have shown that the static ensemble approximation is exact up to third order in the perturbation operator and, thus, is a short time approximation. The approximation, however, involves an infinite series in the perturbation operator such that the limits of very slow and of very fast stochastic modulation as well as the trace of the density matrix are described exactly. The distribution of the time-independent Hamiltonians can be obtained easily and describes the evolution of the stochastic quantum system qualitatively well, even over longer times.

## ACKNOWLEDGMENT

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[16]For a most recent review, see G. L. Closs and J. R. Miller, Science **240**, 440 (1988); the article deals mainly with electron donor–acceptor systems bridged by sterically rigid groups which keep the donor–acceptor distance fixed.
[17]For a general introduction the reader is referred to Refs. 4 and 5.
[18]This notation is only applied to operators which appear in the time as well as the Laplace domain, i.e., $U^x, \tilde{U}^x, \rho, \tilde{\rho}, g$.
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