Probing the dynamics of a polymer with paramagnetic end groups by magnetic fields

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We show that magnetic field effects observed on reactions between two paramagnetic end groups of a polymer can be explained through the folding motion of the polymer. This folding stochastically alters the exchange interaction between the paramagnetic end groups and, thereby, affects their spin dynamics. We describe the resulting stochastic quantum system by a (Monte Carlo) computer simulation as well as by a new approximation which involves the spectrum of the stochastic interaction. This approximation can be of general use for the description of stochastic quantum systems when a diagonal stochastic interaction originates from an arbitrary, i.e., nonlinear and non-Gaussian, stochastic process.

I. INTRODUCTION

The effects of magnetic fields in the range 10–1000 G on reactions between paramagnetic molecules have provided important insights into the dynamics of chemical processes in the condensed phase. In view of the fact that interaction energies giBh for fields in this range are well below thermal energies, the existence of such effects may appear surprising. However, the time scales over which thermodynamic arguments apply is determined by the relaxation times of the paramagnetic materials which can be much longer than the short lifetime $\tau$ of paramagnetic intermediates during a chemical reaction. In this case magnetic fields of the order $B \approx 1/\mu$ can have an influence on the reaction products. For this to be the case the paramagnetic intermediates must be "born" in a pure spin state.

An example of a reaction which is influenced by weak magnetic fields is the light-induced electron transfer reaction involving molecules $^1$A (electron acceptor, e.g., pyrene) and $^1$D (electron donor, e.g., dimethylaniline) which yields "fast" (ns) triplet molecules $^3$A*:

$$^1A + ^1D + \text{photon} \rightarrow ^1A^* + ^1D \rightarrow ^3(A^- + ^2D^+) \rightarrow ^3A^* + ^1D.$$ (1)

Without the partner molecules $^1$D being present "slow" triplets $^3$A* are produced due to spin orbit coupling by the conventional singlet–triplet crossing $^1A^* \rightarrow ^3A^*$. The fast route to triplet molecules Eq. (1) involves the intermediate doublet $^2A^- + ^2D^+$ which is born in an overall singlet state denoted by $^1(A^- + ^2D^+)$. This pure spin state is perturbed by the interactions collected in the Hamiltonian

$$H = H_1 + H_2 + V(J),$$ (2)

$$H_i = \mu_B \cdot B \cdot S_i + \sum_{k=1}^{N_i} a_{ik} I_{ik} \cdot S_i, \quad i = 1, 2,$$ (3)

$$V(J) = J(r) \left[ \frac{1}{2} + 2S_1 \cdot S_2 \right].$$ (4)

$H_i$ describes the interaction of the electron spin $S_i$ of the paramagnetic (doublet) molecule $i$ with the external magnetic field $B$ (Zeeman interaction) and with the $N_i$ nuclear spins $I_{ik}$ (hyperfine interaction). In this article we assume that the $g$ values entering in the Zeeman interaction are both identical and that the hyperfine coupling is isotropic. The hyperfine coupling constants assumed for the compounds pyrene and dimethylaniline are $g$ (in G)

$$\text{pyrene:} \quad 4 \cdot (a_H = 2.3) ; \quad 4 \cdot (a_H = 5.2),$$ (5a)

$$\text{dimethylaniline:} \quad 6 \cdot (a_{CH} = 12.0) ; \quad 1 \cdot (a_N = 12.0); \quad 3 \cdot (a_H = 6.25).$$ (5b)

$V(J)$ represents the exchange interaction which is assumed to act "through space." The coupling strength $J$ depends on the distance between the paramagnetic molecules. Since the exchange interaction acts through the solvent the distance dependence could be influenced by the electronic properties of the solvent molecules. In this article we will adopt the following distance dependence which has been suggested by deKanter et al.:

$$J(r) = J_0 \exp(-ar),$$ (6a)

$$J_0 = 9.46 \times 10^9 \text{ G}, \quad a = 2.136 \text{Å}^{-1}.$$ (6b)

This dependence will play a crucial role in the following and will be further discussed below. For an observation the molecules $^1$A and $^1$D are solvated in a polar organic liquid, for example, methanol. $^1$A is excited electronically by a ns laser flash and the formation of $^3$A* is monitored by a second light beam. The transient concentration of $^3$A* is found to depend strongly on the strength of the external magnetic field $B$. The magnetic field effect can be explained by means of the probability $p_T(t, B)$ that a singlet pair $^1(2A^- + ^2D^+)$ assumes triplet character at time $t$, i.e., reaches the state $^3(2A^- + ^2D^+)$. This probability is given by

$$p_T(t, B) = (1/Z) \text{Tr} \left[ Q_T U(t) Q_S \right],$$ (7)

where

$$Q_S = \frac{1}{2} - S_1 \cdot S_2,$$ (8)

$$Q_T = \frac{1}{2} + S_1 \cdot S_2$$ (9)

are the projection operators on the singlet and triplet states and $U(t)$ describes the propagation of the density matrix of the system. The system is initially in the singlet state as de-
The yield in Fig. 1(a) calculated for a vanishing exchange interaction agrees well with the observations when 1A and 1D are separate molecules which diffuse freely (except for the Coulomb attraction of the doublet pair) in the solvent. A detailed description which accounts for the diffusive motion of the reaction partners 1A− + 1D+ showed that during most of the lifetime \( \tau \) the partners are separated rather far and, hence, the exchange interaction between them is negligible.\(^5\text{,}^9\)

Recently, the formation of fast triplets has been studied for the compound \( 1^A−(\text{CH}_2)_n−1^D\) where 1A and 1D are connected by a short aliphatic polymer chain \((n = 7–16)\).\(^10\text{,}^11\)

In this case the magnetic field dependence appears more like that in Fig. 1(b), i.e., indicates a nonvanishing exchange interaction.

However, the observations in Refs. 10 and 11 show also important differences compared to the yield as shown in Fig. 1(b). First, the maximum value of the yield \( \phi_\tau(B_{\text{max}}) \) is only about 20% larger than the yield \( \phi_\tau(B = 0) \) at zero field. Second, the observed maximum is much broader. These features point to the possibility that the doublet pair \( 1^A−(\text{CH}_2)_n−1^D\) formed as an intermediate experiences a distribution of exchange interactions. In this paper we want to demonstrate that this is, in fact, the case. However, the distribution of exchange interactions which explains the observation does not reflect the static folding pattern of the polymer but rather originates from the dynamics of the folding polymer. The exchange interaction (2) has to be considered a stochastic variable for the doublet pair \( 1^A−(\text{CH}_2)_n−1^D\). We will demonstrate that this compound establishes a prototype stochastic quantum system which is both amenable to a theoretical description and to an experimental observation.

The approach taken below follows two roads: (a) We determine the spin dynamics of the doublet pair by a computer simulation describing as realistically as possible the polymer folding (Sec. II) as well as the spin dynamics (Sec. III). (b) We develop an approximate description (Sec. IV) which involves the spectrum of the stochastic exchange coupling \( J[r(t)] \). This latter approach yields a simple interpretation of the behavior of the stochastic quantum system at least for the case that the lifetime \( \tau \) of the paramagnetic intermediates is short. Both descriptions explain the observed quantum yield \( \phi_\tau(B) \) of the triplet molecules \( 1^A−(\text{CH}_2)_n−1^D \) originating from the paramagnetic polymer intermediate.

The mechanism which leads to magnetic field effects on the reaction (1) is closely related to the mechanism of "chemically induced dynamic polarization" which is observed through changes in the intensities of NMR and ESR spectra of reactants.\(^12\) The influence of the folding of a polymer with paramagnetic ends on NMR spectra has been studied in an important series of papers by de Kanter et al.\(^5\) and by Closs.\(^13\) The papers by de Kanter et al. which provide an explanation of nuclear spin polarizations observed by NMR corroborate our findings presented below. The principal advance achieved in our work is the approximation developed in Sec. IV which leads to a better understanding of the observations. Our theory also addresses an observable different from that in Ref. 6, i.e., the triplet yield \( \phi_\tau(B) \) which is

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**FIG. 1.** Magnetic field dependence of the triplet yield \( \phi_\tau(B) \) of a \( 1^A−(\text{pyrene})− + 1^D\) pair with a lifetime \( \tau = 1 \) ns. (a) \( J = 0 \) G, (b) \( 2J = 300 \) G. The triplet probability has been calculated by spectral expansion of the Hamiltonian \( H \). However, we have adopted the approximation suggested by Eq. (22), with \( n_{i3} = 1 \).

The yield of triplet products \( 1^A \) is then given by

\[
\phi_\tau(B) = \int_0^\infty dt \exp(-t/\tau_0) \rho_\tau(t, B),
\]

where \( \tau_0 \) is the lifetime of the doublet pair \( 1^A− + 1^D\). This observable is shown in Figs. 1(a) and 1(b) for situations with fixed exchange interactions \( J(r) = 0 \) and \( 2J(r) = 300 \) G. The observable has been calculated as described in Ref. 5 and below Fig. 1.

In the case \( J = 0 \) the triplet yield (9) decreases monotonically with increasing magnetic fields and reaches a constant value for fields \( B > \Sigma \alpha \alpha \alpha \). This behavior is well understood.\(^17\text{,}^8\) In the case of a nonvanishing exchange interaction the singlet and triplet levels are energetically shifted with respect to each other by \( 2J \). For \( J > \Sigma \alpha \alpha \alpha \) singlet and triplet transitions cannot be induced by the hyperfine coupling except at fields \( B > 2J \) when for \( J > 0 \) the triplet state \( T_{−1} \) becomes degenerate with the singlet state \( S_0 \). This degeneracy causes the maximum of the triplet yield \( \phi_\tau(B) \) in Fig. 1(b).
produced by transitions involving all four electron spin states. However, an important issue of this work has been to reexamine the theory of deKanter et al. as it is based on the assumption that the exchange interaction \(J\) between the paramagnetic end groups of polymerizes acts "through space" rather than "through bond," the distance dependence of \(J\) being governed by Eq. (6).

The approximation in Sec. IV provides a description of time-dependent stochastic quantum systems in terms of a distribution of time-independent quantum system employing the spectrum of the stochastic interaction. This result is based on the work of Kubo, Johnson, and Blume and allows to describe the influence of nonlinear non-Gaussian stochastic processes on quantum systems, i.e., constitutes a generalization of the description suggested by Anderson and Weiss and Kubo and Tomita. We believe that this approximation is useful beyond the special quantum system considered here.

II. COMPUTER SIMULATION OF THE POLYMER FOLDING

The origin of the stochastic variation of the exchange energy between the paramagnetic end groups of \(\text{A}^-\text{(CH}_2\text{)}_n\text{D}^+\) is the folding of its polymer moiety \(-\text{(CH}_2\text{)}_n\text{A}^-\). The relevant stochastic variable is the distance \(r(t)\) between the two polymer ends. In a "mean field" description the time-dependent distribution of end–end distances \(p(r,t)\) satisfies the Fokker–Planck equation in the strong friction limit:

\[
\frac{\partial}{\partial t} p(r,t) = L(r) p(r,t),
\]

\[
L(r) = D\partial_r\left[ p_0(r) \partial_r^{-1} p_0(r) \right]^{-1}.
\]

Here \(p_0(r)\) denotes the equilibrium distribution function of the end–end distances and \(D\) is the effective diffusion coefficient. The value of which should be somewhat smaller than the constant of diffusion coefficients of the separate groups \(\text{A}^-\) and \(\text{D}^+\). The static distribution \(p_0(r)\) entails information on the sterical interactions of the polymer chain \(-\text{(CH}_2\text{)}_n\text{A}^-\). However, Eqs. (11) and (12) do not correctly describe the effect of the sterical interactions on the polymer dynamics and actually underestimate the longest relaxation times of the system. However, since the life time of the paramagnetic species \(\text{A}^-\text{(CH}_2\text{)}_n\text{D}^+\) of a few nanoseconds is much shorter than the longest relaxation times of the polymer the mean field description adopted here should be sufficient.

In lieu of available information on \(p_0(r)\) we have generated this distribution by a computer simulation which models the force field between all atoms of the system and integrates the Newtonian equations of motion for all degrees of freedom. The simulation program employed has been developed by Karplus and co-workers for the description of the dynamics of biological macromolecules. In our simulation we added random forces and friction to all atoms in order to describe the effect of a solvent. The distribution resulting from sampling the \(r(t)\) values of a long-time trajectory of the polymer is presented in Fig. 2. The diagram shows the actual end–end distribution as it results from the simulation as well as a smooth fit to this distribution in terms of the analytical function

\[
p(r) = r^2(r - r_{\text{max}})^2 \exp[-(1 - r/r_1)^2]
\]

with \(r_{\text{max}} = 11.5\text{ Å}\) and \(r_1 = 25\text{ Å}\). For convenience this latter function was used as \(p_0(r)\) in all further calculations.

The random motion of the end–end distance \(r(t)\) was generated by a Monte Carlo algorithm applied to the stochastic differential equation analog of Eqs. (11) and (12),

\[
dr = D\partial_r \ln[p_0(r)] dt + \sqrt{D} dW_t,
\]

where \(dW_t\) describes white Gaussian noise.

The algorithm generated trajectories \(r(n \tau), n = 0, 1, 2, \ldots\) of end–end distances starting from initial values \(r(0)\) selected according to the equilibrium distribution \(p_0(r)\). The \(n\)th displacement, i.e., \(r[(n – 1) \tau] \rightarrow r(n \tau)\) was chosen according to Eq. (14). For this purpose the force term in Eq. (14) was locally, i.e., around \(r[(n – 1) \tau]\), expanded

\[
D\partial_r \ln[p_0(r)] = \alpha + \beta \{r - r[(n - 1) \tau]\}
\]

and the endpoints \(r(n \tau)\) selected by means of a random number generator from the Gaussian distribution

\[
\{r_0 = r[(n - 1) \tau]\}
\]

\[
dr = (2\pi \sigma^2)^{-1/2} \exp[-\frac{1}{2}(r - \mu)/\sigma]^2
\]

\[
\sigma = [(1 - \theta)^2/\beta]^{1/2}
\]

\[
\mu = r_0 \beta - \alpha (1 - \theta)/\beta
\]

The resulting trajectories \(r(n \tau), n = 0, 1, 2, \ldots\) yield the fluctuating exchange interactions \(J[r(n \tau)]\) which, henceforth, will be denoted by \(J(n \tau)\). It should be noted that \(J(n \tau)\) does not result from white Gaussian noise. A corresponding approximation would be very poor since \(r(t)\) varies over several Å and, hence, \(J(t)\) varies over several orders of magnitude. Actually, the aim of the present paper is to relate the observed \(\phi_r(B)\) and the stochastic process \(J(t)\) modeled as realistically as possible.

![FIG. 2. Distribution of end-end distances for the polymer CH₃(CH₂)ₗCH₃ resulting from a molecular dynamics calculation involving the computer program of Karplus et al. (Ref. 20). The hydrogen atoms in this compound were not explicitly described but only included through an increase of the van der Waals radii of the carbon atoms. These atoms were subjected to random forces and friction according to the algorithm in Ref. 21. Superimposed is a smooth distribution which is a fit of analytical functions of the type (13) to the simulated distribution](image-url)
This latter approximation was tested for fixed $J$ and was found satisfactory for times long enough compared with the assumed lifetimes $\tau$ of the paramagnetic species. The reader should note that since Eq. (20) is applied repeatedly at times $t = r, 2r, 3r, \ldots$, the approximation (20) is related to the well-known relationship

$$\exp(at) = \lim_{m \to \infty} (1 + at/n)^n.$$  

Figures 3(a) and 3(b) compare for two cases of fixed exchange interactions the triplet probability resulting from an exact calculation with the triplet probability of a calculation which evokes Eq. (20). The triplet probabilities are found to be accurate up to $t = 10$ ns, i.e., well beyond the lifetime $\tau_0 = 1$ ns assumed.

For an application to realistic nuclear spin systems like that of $2^-(\text{pyrene})^{+}-(\text{CH}_2)_n^{2-}$ (dimethylaniline)$^+$ with 18 nuclear spins and over $10^6$ different electron–nuclear spin states the calculation as outlined is too time consuming. Therefore, we replaced the hyperfine interaction in Eq. (3) by

$$\tilde{a}_i \sum_{m=1}^{n_i} \tilde{I}_{i,m} \cdot S_i$$  

with a reduced number $n_i < N_i$ of nuclear spins and all hyperfine coupling constants of one molecule identical. The replacement was chosen such that the following sums are kept invariant ($i = 1, 2$):

$$\tilde{a}_i^2 \sum_{m=1}^{n_i} \tilde{I}_{i,m} (\tilde{I}_{i,m} + 1) = \sum_{k=1}^{N_i} a^2_{ik} I_{ik} (I_{ik} + 1).$$  

This choice guarantees that the reduced nuclear spin system for short and intermediate times reproduces the triplet probability $p_T(t, B)$ of the complete system. This property can be derived from the short time expansion$^{24}$ and from the semiclassical approximation$^{25}$ of $p_T(t, B)$ with the latter of which holds for intermediate times. These descriptions of $p_T(t, B)$ show that the dynamics of the system depend solely on the sums in Eq. (22) and not on the individual hyperfine coupling constants. The time period over which the reduced system reproduces the triplet probability of the complete system increases with the number of nuclear spins $n_i$ as demonstrated in Ref. 23. For our present investigation it was found sufficient to choose only one nuclear spin on each molecule. The spin dynamics of the reduced system can be simulated according to the algorithm suggested by Eqs. (18)–(20) if one exploits the additional simplifications resulting from the fact that the reduced system has all hyperfine coupling constants $\tilde{a}_i$ at one molecule identical.$^{5,23}$

The magnetic field dependence of the triplet yield $\phi_T(B)$ resulting for a $2^-(\text{pyrene})^{+}-(\text{CH}_2)_n^{2-}$ (dimethylaniline)$^+$ pair of paramagnetic groups with an end–end equilibrium distribution of Fig. 2 is presented in Fig. 4. In our simulation we have assumed a value of $4 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the diffusion coefficient $D$. The yield shown closely resembles the observation of Refs. 10 and 11 in that the maximum of $\phi_T(B)$ in Fig. 4 is assumed at the field $B_{\text{max}} = 300 \text{ G}$ which compares well with the observation of $B_{\text{max}} = 285 \text{ G}$. The ratio $\phi_T(B_{\text{max}}) / \phi_T(B = 0)$ is found theoretically to be 1.1 and experimentally to be 1.3. These latter values have to be compared with a ratio of 5
obtained if a fixed exchange interaction of $2J = 300$ G is assumed [see Fig. 1(b)]. The good agreement with the observation shows that one can explain the magnetic field dependence of the triplet yield $\phi_T(B)$ in polymethylene-linked donor–acceptor systems with the stochastic modulation of the distance dependent exchange interaction (6b). This finding provides a strong argument against an influence of a “through bond exchange” along the aliphatic chain and appears to settle the dispute about the origin of the exchange interaction in this polymeric system in favor of an exchange straight through the space (solvent) between the end groups. However, there exists still the possibility that the stochastic variation of the dihedral angles of the polymer contributes to the spin motion of the paramagnetic end groups and that, for some fortuitous reason, the distance dependence (6) effectively accounts for the coupling of the through bond exchange interaction to the polymer folding motion. An argument in favor of the latter possibility is the fact that the distance dependence (6) is not based on a rigorous derivation within the model of a “through space” exchange interaction but should be considered a phenomenological relationship which fits the observations in Refs. 6, 10, 11, and 13.

The computer simulation which yielded the results in Fig. 4 is extremely time consuming and demanded a CPU time of about 100 h on a VAX 11/750. This vast amount of computer time is due to the Monte Carlo character of the algorithm which requires large enough samples to produce significant results. The simulation does not yield many insights about the behavior of the stochastic spin system, e.g., does not provide an answer about the question why the maximum of $\phi_T(B)$ is observed at about 300 G. The computer time of the theoretical description can be drastically reduced and insight can be gained if one employs an approximate description presented in Sec. IV.

IV. SPECTRUM OF THE STOCHASTIC EXCHANGE INTERACTION

In this section we seek an approximation of the propagator (18). The fluctuating exchange interaction $J(t)$ and the necessary ensemble averages can be evaluated formally best if one considers the density matrix $\rho (r, t)$ to be a function of the end–end distance $r$. The propagator $U(t)$ operates then on a space $V_1 \otimes V_2$, where $V_1$ is the space of the spin density matrix and $V_2$ is the space of appropriate functions to describe the time-dependent end–end distribution. This operator satisfies the Liouville equation

$$
\partial_t U(t) = \{-iH[J(r)] + L\}U(t),
$$

where $L$ denotes the Fokker–Planck operator (12). The operators are defined here and in the following either in the spaces $V_1$ or in the space $V_1 \otimes V_2$. No difficulty should result from this ambiguity. The Laplace transform of $U(t)$ is

$$
\hat{U}(s) = [s + iH(J) - L]^{-1}.
$$

For the purpose of approximating $U(s)$ we define the spin operators

$$
H[J(t)] = A[J(t)] + \lambda B,
$$

where $A$ describes the diagonal part of $H$ and $B$ the off-diagonal part. $\lambda$ is a parameter which will serve us to examine the approximation developed and is set to $\lambda = 1$ later.

In the basis in which the electron spin pair is coupled to overall singlet or triplet states the exchange and Zeeman part of the Hamiltonian (2) and, hence, of the superoperator $H$ are diagonal. These interactions can be very large and give rise to rapid phase oscillations. The hyperfine interaction is constant and determines the time scale over which the probability for singlet–triplet transitions develops. Hence, we adopt for our approximation a perturbation expansion with $A$ chosen as the (diagonal) unperturbed part and $\lambda B$ as the perturbation. The propagator $U(t)$ defined in Eq. (18) will be developed in powers of $\lambda t$. For this purpose we expand $U(t)$ in powers of $\lambda$.

Before we provide this expansion we note the following properties of $A$ and $B$. If we denote by $P$ the projection operator onto that part of $V_1$ which entails the diagonal elements of the spin density matrix $\rho_n$ then

$$
PA = 0, \quad PA = AP = 0,
$$

(26a)

$$
PBP = 0.
$$

(26b)

Here the indices $r,t$ refer to electron–nuclear spin states with the electron spin in a singlet–triplet basis. We are interested solely in the ensemble averaged $P\hat{U}(s)P$ part of the propagator. The corresponding $\lambda$ expansion is

$$
\langle P\hat{U}(s)P \rangle = s^{-1}P + s^{-2} \sum_{n \geq 1} P \langle \hat{\psi}_n(s) \rangle (-i\lambda B)P,
$$

(27)

$$
\langle \hat{\psi}_n(s) \rangle = \{ -i\lambda B [s + iA(J) - L]^{-1} \}^n.
$$

(28)

We now introduce the approximation

$$
\langle \hat{\psi}_n(s) \rangle \approx \int_0^\infty dj g(j) \{ -i\lambda B [s + iA(j) - L]^{-1} \}^n.
$$

(29)

$$
g(j) = \frac{1}{\pi} \text{Re} \langle [i(2j - 2J) - L]^{-1} \rangle.
$$

(30)

The approximation (29) is a key result of this paper. Its value will be demonstrated by examining in how far it reproduces the exact evolution operator. We first note that the approximation (27)–(30) is exact to order $\lambda$.

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FIG. 5. Spectrum $q(j)$ of the exchange interaction as defined in Eq. (30); (a) for $D = 0$ [see Eq. (32)]; (b) $D = 4\times 10^{-6}$ cm$^2$s$^{-1}$; (c) $D = 4\times 10^{-3}$ cm$^2$s$^{-1}$; (d) $D = 4\times 10^{-4}$ cm$^2$s$^{-1}$.

\[
\int_{-\infty}^{\infty} dj \, q(j) \left[ s + i(\alpha + \beta 2j) \right]^{-1} = \left( \left\{ s + i(\alpha + \beta 2j) - L \right\}^{-1} \right) \tag{31}
\]

with $\beta = 0, \pm 1$ and from the fact that $J(r)$ enters only in the form $\beta 2J(r)$ in A(J). For $\lambda^3$ it follows from the fact that in $\delta_0(s)$ the exchange interaction enters at most twice, however, always with the same prefactor.28 This observation shows that the approximation holds exactly for short times, the time scale being defined by the strength of the hyperfine coupling, not the exchange and Zeeman interactions. One can expect that the approximation suggested results in exact triplet yields $\phi_T(B)$ as long as the lifetime $\tau$ is only a few nanoseconds. However, the approximation provides a qualitatively correct magnetic field dependence of $\phi_T(B)$ also for longer lifetimes.28 This is possible since the approximation (27)–(30) does not correspond to a perturbation series in $\lambda$ terminated after $\lambda^3$ terms, but rather entails partial infinite sums, i.e., terms to all orders in $\lambda$.

The infinite series contributions taken into account are chosen such that the approximation (29) holds exactly for long times in case of either very slow or very fast stochastic motion of $r(t)$, i.e., for Fokker–Planck operators with either very small or very large nonvanishing negative eigenvalues. This is trivial for the case of slow polymer folding. The distribution of $j$ values is in this case $q(j) = p_0[r(J)] \frac{dr}{dj}$. \tag{32}

For the case of very fast motion the distribution $q(j)$ assumes the motional narrowing limit,14 i.e.,

\[
q(j) = \delta(j - \langle J \rangle); \quad \langle J \rangle = \int_{-\infty}^{\infty} dr \, p_0(r) J(r). \tag{33}
\]

In this situation only a “single” exchange interaction affects the spin motion, i.e., $J$ is effectively time independent and Eq. (29) holds exactly.

The approximation introduced in this section can be cast into the form

\[
U(t) \approx \int_{-\infty}^{\infty} dj \, q(j) \exp[ -it \mathbf{H}(j) ], \tag{34}
\]

where the propagator $U(t)$ with a time-dependent (stochastic) superoperator $\mathbf{H}[J(t)]$ is replaced by a superposition of propagators $\exp[ -it \mathbf{H}(j) ]$ with time-independent superoperators $\mathbf{H}(j)$. Here $\mathbf{H}(j)$ denotes the same superoperator as $\mathbf{H}[J(t)]$ except that the stochastic exchange interaction $J(t)$ is replaced by the constant $J$. Equation (34) implies that the spectrum $q(j)$ defined in Eq. (30) can be interpreted as a dynamical distribution of exchange interactions $j$ of the polymer system. This distribution is shown in Fig. 5 for the four cases $D = 0, 4\times 10^{-6}, 4\times 10^{-3}$, and $4\times 10^{-4}$ cm$^2$s$^{-1}$.
The algorithm employed for the numerical evaluation of \( q(j) \) from Eq. (30) involves the discretization of the operator in Eq. (31) as described in Refs. 6 and 29 and application of the Gauss–Seidel algorithm to determine the inverse of a tridiagonal matrix.  

The different distributions in Fig. 5 show that the folding dynamics shift the spectrum of exchange interactions from small values for \( D = 0 \) to larger values for increasing \( D \). In case \( D = 0 \) and \( D \to \infty \) the distribution assumes the limits (32) and (33), respectively.

Figure 4 compares the magnetic field dependence of the triplet yield \( \phi_T(B) \) obtained by means of the approximation introduced in this section with the results from the simulation discussed in Sec. III. The agreement found is satisfactory. This implies that an interpretation of the observed triplet yield (which also closely resembles the curve in Fig. 4) should refer to the spectrum of exchange interactions \( q(j) \). The maximum of \( \phi_T(B) \) does indeed occur approximately at the field \( B_{\text{max}} = 2 q_{\text{max}} \), which corresponds to the maximum \( q(j_{\text{max}}) \) of \( q(j) \) as can be seen from a comparison of Fig. 4 and Fig. 5(b). Therefore, the spectrum \( q(j) \) relates the magnetic field effect of \( \phi_T(B) \) to the folding dynamics of the polymer. The approximation (34) can be employed to study the dependence of \( \phi_T(B) \) on the polymer length. The results of such calculations compare well with the available observations.  

Finally we like to express our belief that the approximation (34) of the ensemble propagator can be applied to other stochastic quantum systems as well. This application provides a description when the stochastic interaction is due to a single fluctuating variable. The coupling to this variable must not necessarily be linear and the variable must not originate from a Gaussian process. The approximation introduced is exact in the limits of fast and slow stochastic motion but, in general, holds only exactly to order \( O(\gamma t^3) \) when \( \gamma \) is the coupling constant describing the strength of the off-diagonal part of the quantum process under consideration.

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