Influence of Subdiffusive Motion on Spin Relaxation and Spin Effects in Radical Pairs

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Specific features of spin relaxation and the kinetics of spin effect generation in radical pairs (RPs) undergoing subdiffusive relative motion are studied in detail. Two types of processes are analyzed: (1) spin relaxation in biradicals, resulting from anomalously slow subdiffuisive reorientation (with the correlation function $P(t) \sim (wt)^{-\alpha}$, where $0 < \alpha < 1$) and (2) spin effect generation in subdiffusion-assisted RP recombination. Analysis is made with the use of the non-Markovian stochastic Liouville equation (SLE) derived within the continuous time random walk approach. The SLE predicts anomalous (very slow and nonexponential) spin relaxation in biradicals which results in some peculiarities of the spectrum of the system. In RP recombination, the subdiffusive relative motion shows itself in slow dependence of the reaction yield Y_r on reactivity and parameters of the RP spin Hamiltonian and anomalous electron spin polarization of escaped radicals. The spectrum of the reaction yield detected magnetic resonance, that is, the Y_r dependence on the frequency ω of microwave field, is found to be strongly non-Lorenzian with the width determined by the field strength ω_1 and very broad wings depending on α. Analysis shows that the majority of interesting, specific features of the observables in both systems are controlled only by the parameter α.

I. Introduction

Spin−lattice relaxation and spin effects are the well-known phenomena in the condensed-phase processes involving paramagnetic particles, for example, radicals.[1−4] They result from spin-dependent interactions between these particles, strongly fluctuating because of the stochastic relative motion of the particles.

The methods of describing the manifestations of these fluctuating interactions are well developed and discussed in detail in many books and reviews (see, for example, refs 1 and 5). A very large number of them are based on the conventional short correlation time (SCT) approximation[1] which leads to Bloch-type equations for the spin density matrix. To treat the problem outside the conventional SCT limit, different methods have been proposed. One of them rests on the Zwanzig projection operator formalism.[5] Unfortunately, this formalism, leading to formally exact expressions, is not of great use for applications because it includes all the complexity of statistical physics. Really, tractable formulas can be obtained only within additional approximations. Another method which enables one to make important steps beyond the SCT limit is based on the semiclassical stochastic Liouville equation (SLE) for the density matrix of the system.[6] The strong limitation of the SLE approach consists of classical treatment of the bath. At the same time, unlike the Zwanzig formalism, the SLE approach is exact and, therefore, is free of a number of above-mentioned drawbacks of this formalism. Note the second significant limitation of the SLE, important for this work, results from the assumption that the interaction fluctuations are Markovian.

Recently, close interest to the effects of non-Markovian (with long memory) interaction fluctuations on relaxation in quantum systems has been excited by investigations of processes governed by noises whose correlation functions $P(t)$ decay anomalously slowly: $P(t) \sim t^{-\alpha}$ with $\alpha < 1$. One of the most actively discussed examples of such noises are those controlled by anomalous diffusion (subdiffusion) for which the mean square displacement $\langle r^2(t)\rangle \sim t^{\alpha}$.[8]

A number of phenomena, in which anomalous processes play important role, are discussed in the literature.[7,8] Some of them are analyzed in relation to spectroscopic studies of quantum dots.[9,10] Similar problems are considered in the classical theory of dielectric relaxation[11] (and references therein). All anomalous relaxation processes mentioned above cannot be properly described within the conventional SCT limit. The conventional SLE approach is not appropriate either.

The efficient method of analyzing the memory effects is based on the continuous time random walk (CTRW) approach.[12−14] Within this approach, one can derive the non-Markovian variant of SLE[15,16] which appeared to be very fruitful for describing memory effects on some classical and quantum processes assisted by stochastic anomalous spatial migration.[17,18]

In this work, the non-Markovian SLE is applied to the analysis of specific features of spin relaxation and magnetic field (spin) effects[2−4] in radical pairs undergoing subdiffusive relative motion. As an example of relaxation processes, we will discuss spin relaxation in biradicals with special attention concentrated on the limit of short characteristic time (of type of correlation time), describing an anomalous stochastic reorientation process. In this limit, the kinetics of anomalous quantum relaxation in biradicals (induced by this reorientation) appears to be independent of the particular model of orientational relaxation,[18] demonstrating some interesting specific features. As for magnetic field (spin) effects in radical pair recombination assisted by relative subdiffusion, they are also shown to have some important specific features resulting from the anomalous character of relative motion (associated with the anomalously long memory effects in the system): nonanalytical dependence of magnetic field affected recombination yield (MARY) and chemically induced dynamic electron polarization (CIDEP) on the parameters of the spin Hamiltonian, strongly non-Lorenzian shape of lines of reaction yield detected magnetic resonance

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(RYDMR), etc. The obtained specific features of various observables can be used for the identification and analysis of the anomalous motion of radicals in inhomogeneous media.

II. General Formulation

We consider relaxation in the quantum system induced by quantum noise and fluctuating irreversible first-order processes (the state-dependent decay, etc.). Evolution of the system is described by the density matrix $\rho(t)$ satisfying the Liouville equation. In the absence of irreversible first-order processes, it is written as ($\hbar = 1$)

$$\dot{\rho} = -i\hat{H}(t)\rho \quad \text{with } \hat{H}\rho = H\rho - \rho H \tag{2.1}$$

Here

$$H(t) = H_s + V(t) \tag{2.2}$$

is the Hamiltonian in which H_s is the term independent of time and $V(t)$ is the fluctuating interaction, assumed to be symmetric ($\langle V\rangle = 0$) and resulting from stochastic jumps between the states $|r_\nu\rangle$ in the (discrete or continuum) space $\{r_\nu\} \equiv \{r\}$ with different $V = V_\nu$ and $H = H_\nu$ (i.e., different $\hat{V} = \hat{V}_\nu \equiv [V_\nu, ...]$ and $\hat{H} = \hat{H}_\nu$)

$$\hat{V} = \sum_\nu |r_\nu\rangle \hat{V}_\nu \langle r_\nu|$$

and

$$\hat{H} = \sum_\nu |r_\nu\rangle \hat{H}_\nu \langle r_\nu| \tag{2.3}$$

Hereafter, we will apply bra-ket notation

$$|k\rangle, \quad |kk'\rangle \equiv |k\rangle\langle k'|, \quad \text{and } |r\rangle \tag{2.4}$$

for states in the Hilbert space (for H), in the Liouville space (for $\hat{H}$), and in $\{r\}$ space, respectively.

The effect of the above-mentioned irreversible first-order processes can be described by the non-Hermitian "reactivity" operator $-i\hat{K}$ in the Liouville space so that, in general, the Liouville equation can be represented as

$$\dot{\rho} = -i\hat{L}\rho, \quad \text{in which } \hat{L} = \hat{H} - i\hat{K} \tag{2.5}$$

It is worth mentioning that the effect of the "reactivity" $i\hat{K}$ can, in principle, lead to a violation in the positivity of $\hat{G}$. However, there are some particular forms of this operator that are known to ensure the positivity.[2] One of them, $i\hat{K}\rho = \kappa\{P_\kappa,\rho\} = \kappa(P_\kappa\rho + \rho P_\kappa)$, where P_κ is the operator of projection onto the reaction state $|\kappa\rangle$, will be applied in our work.

The time evolution of observables under study is determined by the evolution operator $\hat{R}(t)$ in the Liouville space averaged over $V(t)$ and $K(t)$ fluctuations

$$\rho(t) = \hat{R}(t)\rho_i \quad \text{where } \hat{R}(t) = \langle T e^{-i\int_0^t d\tau \hat{L}(\tau)}\rangle \tag{2.6}$$

The operator $\hat{R}(t)$ can equivalently be represented in terms of the conditional evolution operator $\hat{G}(r,r'|\, t)$ averaged over the initial distribution $P_i(r)$

$$\hat{R}(t) = \langle \hat{G}\rangle \equiv \sum_{r,r_i} \hat{G}(r,r_i|t)P_i(r_i) \tag{2.7}$$

Note that for steady-state $V(t)$ fluctuations $P_i(r) = P_e(r)$, where $P_e(r)$ is the equilibrium distribution. For some processes, however, the observables are expressed in terms of the operator $\hat{G}(r,r_i|t)$ itself rather than $\hat{R}(t)$ (see section IVC).

III. Non-Markovian Stochastic Liouville Equations

Continuous Time Random Walk Approach. Non-Markovian $V(t)$ and $\hat{K}(t)$ fluctuations can conveniently be described by the CTRW approach treating them as a sequence of changes of $\hat{V}$ and $\hat{K}$. The onset of the jth change is described by the diagonal matrix $\hat{P}_{j-1}$ (in $\{r\}$ space) of probabilities not to have any change during time t and its derivative $\hat{W}_{j-1}(t) = -d\hat{P}_{j-1}(t)/dt$, that is, the probability distribution matrix for times of waiting for the change

$$\hat{P}_{j-1}(t) = \hat{P}(t) \quad (j > 1) \quad \hat{P}_0(t) \equiv \hat{P}_i(t) \tag{3.1}$$

so that $\hat{W}_{j-1}(t) = \hat{W}(t) = -d\hat{P}(t)/dt$ and $\hat{W}_0(t) \equiv \hat{W}_i(t) = -d\hat{P}_i(t)/dt$. The matrices $\hat{P}_i(t)$ and $\hat{W}_i(t)$ depend on the problem considered. For example, for nonstationary (n) fluctuations[12−14]

$$\hat{W}_i(t) = \hat{W}_n(t) = \hat{W}(t) \tag{3.2}$$

In the case of stationary (s) fluctuations, $\hat{W}_i(t) = \hat{W}_s(t) = \hat{\tau}_e^{-1} \int_t^\infty d\tau\, \hat{W}(\tau)$ with $\hat{\tau}_e = \int_0^\infty dt\, t\hat{W}(t)$.[12−14]

It is worth noting useful relations for the Laplace transforms of $\hat{W}_j(t)$ and $\hat{P}_j(t)$: $\tilde{P}_j(\epsilon) = [1 - \tilde{W}_j(\epsilon)]/\epsilon$ and

$$\tilde{W}(\epsilon) = [1 + \hat{\Phi}(\epsilon)]^{-1} \quad \tilde{P}(\epsilon) = [\epsilon + \epsilon/\hat{\Phi}(\epsilon)]^{-1} \tag{3.3}$$

where $\hat{\Phi}(\epsilon)$ is the auxiliary matrix diagonal in $\{r\}$ space.

Stochastic Liouville Equation. The time evolution of quantum systems with fluctuating interactions is completely described by the conditional evolution operator $\hat{G}(r,r'|t)$. The CTRW approach allows one to derive the equation for this operator which is called hereafter non-Markovian SLE.[15,16] In what follows, we will discuss the SLE in the form proposed in ref 16, which is much more suitable for our further general analysis and especially for considering anomalous relaxation processes. The non-Markovian SLE is conveniently represented in the resolvent form for the Laplace transform $\tilde{G}(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t}\hat{G}(t)$[15,16]

$$\tilde{G} = \tilde{P}_i + \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Omega})[\hat{\Phi}(\hat{\Omega}) + \hat{L}]^{-1}\hat{P}\tilde{W}_i \tag{3.4}$$

where $\hat{\Omega} = \epsilon + i\hat{L}$. In eq 3.4, $\tilde{P}_i$ and $\tilde{W}_i$ are the Laplace transforms of the initial probability distribution matrices defined in eq 3.1 and $\hat{\Phi}(\hat{\Omega})$ is the matrix which characterizes $\hat{W}(t) = \hat{W}_n(t)$ (see eq 3.3).

The operator $\hat{L}$ describes jump-like radical motion. For simplicity, we will assume that one of the radicals undergoes isotropic diffusion in three-dimensional $\{\mathbf{r}\}$ space, while the second radical does not move and is located at $\mathbf{r} = 0$. In this model[16]

$$\hat{L} = \hat{L}_D = -\lambda^2 r^{-2}\nabla_r[r^2(\nabla_r + \nabla_r u_r)] \tag{3.5}$$

where $r = |\mathbf{r}|$, $\nabla_r = \partial/\partial r$ is the gradient operator, λ^2 is the average square of the jump length independent of r, and u_r is the external interaction potential.

The potential u_r is assumed to be the deep spherical well of radius R much larger than the distance d of closest approach of radicals: $u_r = -u_0\theta(R - r)$ with $u_0 \gg 1$.

Noteworthy is that in this continuum model of stochastic jumps $\hat{V}$ and $\hat{K}$ are just functions of r

$$\hat{V} = \sum_r |r\rangle \hat{V}_r \langle r| \quad \text{and} \quad \hat{K} = \sum_r |r\rangle \hat{K}_r \langle r| \tag{3.6}$$

If operator $\hat{L}$ (eq 3.5) has the equilibrium eigenstate $|e_r\rangle = \sum_r P_e(r)|r\rangle$ (and $\langle e_r| = \sum_r \langle r|$) for which $\hat{L}|e_r\rangle = 0$, then the system relaxes to this state.

In our analysis, we will concentrate on anomalous interaction fluctuations which are often modeled by[8,16]

$$\hat{\Phi}(\epsilon) = (\epsilon/w)^{\alpha} \quad (0 < \alpha < 1) \tag{3.7}$$

where w is the important rate parameter which determines the characteristic time w^{-1} of correlations of interaction fluctuations. Formula 3.7 presents the simplest variant of the model describing anomalously slow decay of the probability distribution matrix[8] with $P(t) = E_{\alpha}[-(wt)^{\alpha}]$ and

$$\hat{W}(t) = -\dot{E}_{\alpha}[-(wt)^{\alpha}] \sim 1/t^{1+\alpha} \tag{3.8}$$

where $E_{\alpha}(-x) = (2\pi i)^{-1} \int_{-i\infty}^{i\infty} dx(z + xz^{1-\alpha})^{-1}e^z$ is the Mittag–Leffler function.[19] It is easily seen that this anomalous type of the CTRW approach cannot be characterized by any average time and, therefore, for model 3.7, only the nonstationary (n) variant of the CTRW is physically sensible.

Note that for any initial state $|i_r\rangle = \sum_r P_i(r)|r\rangle$ the average of some operator $\hat{Y}$ can be represented as $\langle \hat{Y}\rangle_i = \langle e_r|\hat{Y}|i_r\rangle$. In particular (see eq 2.7)

$$\hat{R}(t) = \langle e_r|\hat{G}|i_r\rangle \equiv \langle \hat{G}\rangle_i \tag{3.9}$$

According to eq 3.4, the initial state $|i\rangle$ manifests itself only in the expressions for matrices $\hat{W}_i(t)$ and $\hat{P}_i(t)$. For example, in the nonstationary n-CTRW approach, which is of main interest for this analysis, $|i\rangle = |t\rangle^{12-14}$ so that $\tilde{W}_i = \tilde{W}_n$, $\tilde{P}_i = \tilde{P}_n$, and

$$\tilde{G}(\epsilon) = \tilde{G}_n(\epsilon) = \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Omega})[\hat{\Phi}(\hat{\Omega}) + \hat{L}]^{-1} \tag{3.10}$$

IV. Applications and Discussion

Here, we will apply the general formulas presented above to two types of processes: transversal spin relaxation (dephasing) in biradicals (as applied to the ESR line shape) and spin effects in RP recombination in liquids, which will be analyzed to illustrate the obtained general results.

A. Relaxation in Biradicals. 1. Formulation of the Model. Interaction. In accordance with the conventional formulation,[1] we will consider spin relaxation in biradicals in the strong magnetic field B. The biradical is modeled as a pair of pointlike paramagnetic particles with electron spins of 1/2, $\mathbf{S}_a$ and $\mathbf{S}_b$, located at a fixed interparticle distance r_0 in the strong magnetic field B. Dephasing (transversal relaxation) results from the modulation of the Zeeman levels caused by the fluctuating magnetic dipole–dipole interaction.[1] This process is described by the Hamiltonian[1]

$$H_s = -\omega_s(S_{az} + S_{bz}) + V(t) \tag{4.1}$$

in which

$$V = \omega_d(\cos^2\theta - 1/3)(3S_{az}S_{bz} - \mathbf{S}_a\mathbf{S}_b) \tag{4.2}$$

where $\omega_d = (3/4)b^{-3}\hbar\gamma^2$ and $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio. The fluctuations of V are assumed to be governed by orientational relaxation of the biradical resulting in fluctuations of the angle θ between the vector $\mathbf{b}$ of the relative position of radicals and the $\mathbf{z}$ direction of the external magnetic field B.[1]

Model of Orientational Relaxation. The problem of the study of spin relaxation kinetics and the evaluation of ESR line shape reduces to solving the complicated SLE (eq 3.4) corresponding to anomalous relative orientational motion of biradicals. Analytically this can be done within a number of approaches, for example, subdiffusion (with $\hat{L}$ defined in eq 3.5) or sudden reorientation models.[15,18] Earlier considerations[21] demonstrated that both these types of models reproduced quite well all conventional specific features of dephasing in biradicals.

We are not going to analyze in detail different models of orientational relaxation but restrict ourselves to the demonstration (as an example) of the simple expression for $\tilde{R}$ in the sudden reorientation model: $\tilde{R} = \tilde{R}_n = \langle \tilde{P}\rangle[1 - \langle \tilde{W}\rangle]^{-1}$. This expression enables one to easily obtain a formula for $\tilde{R}_n$ in the limit of short characteristic time w^{-1} of anomalous orientational relaxation.[18] The limiting formula is, in fact, independent of the mechanism of reorientation and is of main interest for our further analysis.

It is important to note that, in the case of anomalous reorientation statistics (with the correlation function $P(t) \sim 1/t^{\alpha}$ ($\alpha < 1$)) such as that predicted by model 3.8, w^{-1} cannot be treated as the correlation time. Actually, in this model, the correlation (average) time does not exist. This peculiarity of the anomalous reorientations results in a very unusual behavior for the relaxation kinetics in the quantum system in the limit of short w^{-1} (see below).

Spectrum. In the considered case of anomalous interaction fluctuations, the biradical spectrum $I(\omega)$ cannot be defined by the conventional formula in terms of the Fourier transformation of the correlation function because it appeals to the Wiener–Khinchin relation which is not valid for anomalously slow $V(t)$ interaction fluctuations. The relaxation properties of such anomalous systems can be analyzed with the use of the anomalous spectrum measured by Fourier transformed free induction decay (FTFID) experiments[20] $I(\omega) \sim \int_0^{\infty} dt \cos(\omega t)\langle S_x(t)\rangle$, where S_x is the x component of the spin. For considered anomalous fluctuations, this spectrum represents the generalization of the conventional one. For the system under study, the anomalous FTFID spectrum is written as follows

$$I(\omega) = \frac{1}{\pi} Re\langle ss|\tilde{R}(i\omega)|ss\rangle \tag{4.3}$$

where

$$|ss\rangle = \frac{1}{\sqrt{2}}\,|T_+T_0\rangle + |T_-T_0\rangle\rangle \tag{4.4}$$

2. Results. In our analysis of the biradical spectrum, we will restrict ourselves to the limit of short effective correlation time w^{-1} of fluctuations (see eq 3.7) in which $\omega_d/w \ll 1$. The SCT limit is of special interest because in this limit any conventional Markovian (diffusion or sudden reorientation type) models of orientational relaxation predict the collapse of the spectrum, that is, the transformation to the δ-function-like one at the center of the spectrum.[1,21] At the same time, in anomalous non-Markovian models (with the CTRW reorientation statistics, described by eqs 3.3 and 3.7), the limiting spectrum is incomparably less trivial. The corresponding specific features of anomalous non-Markovian reorientation mechanism manifest themselves not only in dephasing (and, therefore, in spectrum) but also in population relaxation.[18]

Some interesting unusual properties of anomalous relaxation caused by anomalous non-Markovian reorientation can easily be demonstrated even with the general expression for the evolution operator, which in the anomalous SCT limit ($\omega_d/w \ll 1$) is represented as[18]

$$\tilde{R}(\epsilon) \approx \tilde{R}_n(\epsilon) \approx \langle \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Omega})\rangle / \langle \hat{\Phi}(\hat{\Omega})\rangle \tag{4.5}$$

The most important property consists in nontrivial form of this operator, which is independent of the characteristic time w^{-1} and is only determined by the anomalous exponent α (see eqs 3.7 and 3.8).

Note, in addition, that the expression 4.5 is quite universal: it is valid for any mechanism of anomalous orientational relaxation of subdiffusion or sudden reorientation type. The only feature implied in the derivation of this expression is the slow asymptotic long time behavior of $W(t) \sim 1/t^{1+\alpha}$. Furthermore, the analysis of formula 4.5 with the Markovian representation for the anomalous CTRW processes[16] shows that the formula is valid for a large variety of the initial waiting-time distribution $W_i(t)$ (see section III) of the nonstationary CTRW process.

To obtain the spectrum $I(\omega)$, one should substitute the expression 4.5 into eq 4.3. After simple algebra, one arrives at

$$I(x) = \frac{1}{2}[I_0(x) + I_0(-x)] \quad \text{with } x = (\omega - \omega_s)/\omega_d \tag{4.6}$$

Here, $I_0(x)$ is given by formula

$$I_0(x) = \frac{\sin\varphi_0}{\pi}\frac{\psi_-^{\alpha}\,\psi_+^{\alpha-1} + \psi_-^{\alpha-1}\,\psi_+^{\alpha}}{(\psi_-^{\alpha})^2 + (\psi_+^{\alpha})^2 + 2\psi_-^{\alpha}\,\psi_+^{\alpha}\cos\varphi_0} \tag{4.7}$$

in which $\varphi_0 = \pi\alpha$ and

$$\begin{aligned}\psi_-^{\beta} &= \langle |x - V/\omega_d|^{\beta}\theta(x - V/\omega_d)\rangle_V \\ &= (1-x)^{\beta+1/2}B(1/2, 1+\beta)\end{aligned} \tag{4.8}$$

$$\begin{aligned}\psi_+^{\beta} &= \langle |x - V/\omega_d|^{\beta}\theta(V/\omega_d - x)\rangle_V \\ &= \psi_+^{\beta}(x)\int_1^{u(x)} \mathrm{d}v\,(v^2-1)^{\beta}\end{aligned} \tag{4.9}$$

where $\theta(x)$ is the Heaviside step function, $B(y,z)$ is Euler's β function,[22] and $u(x) = (3/(1-x))^{1/2}$.

The anomalous biradical spectrum evaluated with eq 4.6 for different values of $\alpha < 1$ is shown in Figure 1. In general, specific features of the shape of this spectrum $I(x)$ are significantly different from those of the conventional spectrum (observed in the case of reorientation relaxation resulting from conventional rotational diffusion):[1]

(1) $I(x)$ is confined in the region $-2 < x_d < 2$; as α increases from 0 to 1, the spectrum changes from the quasistatic one to that of Lorenzian shape with the width $w_s \sim (1-\alpha)\omega_d$ at $1 - \alpha \ll 1$. The central peak appears at $\alpha = \alpha_s \approx 0.32$.

(2) Unlike the conventional spectrum, for $\alpha < 1/2$ the anomalous spectrum $I(x)$ is singular at $x = \pm 1$: at $|x| < 1$ and $1 - |x| \ll 1$, $I(x) \sim (1 - |x|)^{\alpha - 1/2}$.

(3) As $\alpha \to 1$, the spectrum $I(x)$ reduces to the Lorenzian one (similar to the case of the two-level system[10,18]) with the

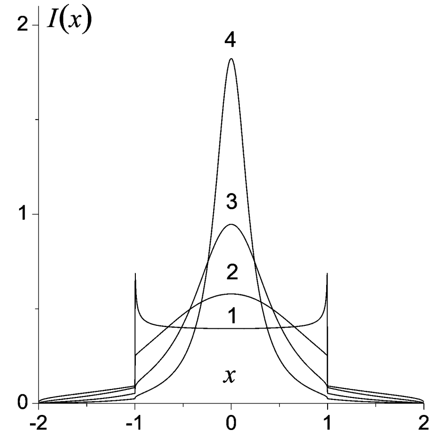

Figure 1. Biradical ESR spectrum $I(x)$, where $x = \omega/\omega_d$, calculated in model 4.2 (using eq 4.6) for different values of α: (1) $\alpha = 0.3$, (2) $\alpha = 0.5$, (3) $\alpha = 0.7$, and (4) $\alpha = 0.85$.

width w_L decreasing as $w_L \sim w_d(1-\alpha)$.[18] Note that, unlike the Lorenzian spectrum in the conventional narrowing limit,[1] the anomalous spectrum (eq 4.6) for $\alpha \to 1$ has the width w_L independent of the characteristic time w^{-1}. For α approaching 1, the spectrum $I(x) \to \Delta(x)$, as it is expected for Markovian fluctuations with $w \to \infty$.

This brief discussion of the anomalous spectrum shows that its peculiarities are fairly pronounced and can, probably, be observed experimentally. In the case of finite effective correlation time w^{-1}, the above-mentioned singularities of the anomalous spectrum $I(x)$ will, of course, be partially smoothed but, nevertheless, the most important specific features of $I(x)$, such as very pronounced shoulders at $x \sim \pm 1$, are expected to persist.

B. Radical Pair Recombination. The spin (magnetic field) effect on reactions of paramagnetic particles undergoing subdiffusive relative motion is another interesting example of processes in which the manifestation of anomalously long memory (associated with an anomalous (subdiffusive) type of motion) in observables is expected to be markedly strong. In this work, we will consider spin effects in radical pair recombination.

It is worth noting that the anomalous SLE which describes spin effects turns out to be fairly close to the conventional one in its mathematical form and, therefore, the corresponding anomalous expressions for amplitudes of spin effects can be obtained by clear and simple modifications of the conventional ones. This will allow us to analyze a number of anomalous effects of different types by analogy with the corresponding conventional effects.

1. Formulation of the Model. Interaction between Radicals. To demonstrate the most important specific features of anomalous spin effect on subdiffusion-assisted radical pair recombination, we will restrict ourselves to the analysis of simple effects observed in the strong magnetic field **B** for which the Zeeman interaction is much larger than intraradical interactions (hyperfine interaction, etc.) but will also consider the effect of the external microwave field B_1 rotating with the frequency ω in the plane perpendicular to **B**.

For strong magnetic fields (in the presence of the field B_1), the spin Hamiltonian governing the evolution of electron spins $\mathbf{S}_a$ and $\mathbf{S}_b$ of radicals, denoted as a and b, can conveniently be written in the frame of reference rotating around **B** with the frequency ω[4]

$$H_r = H_z^0 + J_r \tag{4.10}$$

In this equation, the last term is the exchange interaction

$$J_r = J_0 e^{-\alpha_{ex}(r-d)}\left(\frac{1}{2} + 2\mathbf{S}_a\mathbf{S}_b\right) \tag{4.11}$$

and

$$H_z^{\ 0} = H_a + H_b \tag{4.12}$$

is the Zeeman part, which is a sum of two ones defined as

$$H_\mu = (\omega_\mu - \omega)S_{\mu z} + \omega_1 S_{\mu x} \quad (\mu = a, b) \tag{4.13}$$

where $\omega_\mu = g_\mu\beta B + \sum_j A_j^\mu I_{jz}$ is the Zeeman frequency of the radical μ possessing some paramagnetic nuclei with hyperfine interactions A_j^μ and $\omega_1 \approx 1/2(g_a + g_b)\beta B_1$. The Hamiltonian (eq 4.10) operates in the space of radical pair spin states $|\pm\rangle_a|\pm\rangle_b$ or in the space of eigenstates of the total spin $\mathbf{S} = \mathbf{S}_a + \mathbf{S}_b$: $|S\rangle = 1/(2)^{1/2}(|+\rangle_a|-\rangle_b - |-\rangle_a|+\rangle_b)$, $|T_0\rangle = 1/(2)^{1/2}(|+\rangle_a|-\rangle_b + |-\rangle_a|+\rangle_b)$, and $|T\pm\rangle = |\pm\rangle_a|\pm\rangle_b$.

In the absence of the microwave field, the evolution is still described by the spin Hamiltonian (eq 4.10) but with $\omega_1 = 0$ and $\omega = 0$.

Radical pair recombination can be treated as a contact reaction at a distance of closest approach d using the following simple model[4]

$$\hat{K}_r = k_0\hat{\kappa}_S\theta(r - d)\theta(d + \Delta - r) \tag{4.14}$$

where $\hat{\kappa}_S = \{P_s, ...\}$ is the anticommutator ($\{P_s,\rho\} = P_s\rho + \rho P_s$) in which $P_s = |S\rangle\langle S|$ is the operator of projection on the singlet ($|S\rangle$) radical pair spin state.

The radical pair is assumed to be initially created in the $|S\rangle$ state within the well u_r at a distance r_i, $d < r_i < R$, so that

$$\rho(r,t=0) \equiv \rho_i(r) = (4\pi r_i^{\ 2})^{-1}\delta(r - r_i)P_s \tag{4.15}$$

Spin Effect Observables. In experiments on spin effects, a number of observables are discussed.[4] Here, we analyze the most simple ones:

(1) Two of the most popular are MARY[4] and RYDMR.[4] In both types of experiments, the observables under study are recombination (Y_r) and dissociation (Y_d) yields

$$Y_r = 1 - Y_d = (d/r_i)^2\Delta k_0 Tr[P_s\tilde{G}(d, r_i|\epsilon = 0)P_s] \tag{4.16}$$

Naturally, formula 4.16 should be averaged over nuclear configuration (over ω_μ). However, in our further discussion, we will omit this procedure and analyze the behavior of Y_r for fixed ω_a and ω_b (as in radical pairs without paramagnetic nuclei).

(2) Another well-known type of magnetic field effects is multiplet CIDEP determined as[2]

$$Y_e = \lim_{\epsilon\to 0}\epsilon\int_{r>d} d^3r\ Tr[S_a\tilde{G}(d, r_i|\epsilon)P_s] \tag{4.17}$$

2. Anomalous SLE. Subdiffusion of the mobile radical of the radical pair (recall that the second radical is assumed to be immobile) leads to nonstationary fluctuations of $\hat{K}_r$ and $\hat{H}_r$. The effect of them is described by the operator $\tilde{G}(r,r_i|\epsilon)$ satisfying the non-Markovian SLE (eq 3.10)

$$\hat{\Omega}_r\tilde{G} = -\hat{L}_D(\tilde{M}_r\tilde{G}) + (4\pi r_i^{\ 2})^{-1}\delta(r - r_i) \tag{4.18}$$

where $\hat{\Omega}_r = \epsilon + \hat{K}_r + i\hat{H}_r$ and $\tilde{M}_r = \hat{\Omega}_r/\Phi(\hat{\Omega}_r) = w(\hat{\Omega}_r/w)^{1-\alpha}$.

In general, the solution of eq 4.18 with the Smoluchowski operator $\hat{L}_D$ (eq 3.5) is fairly complex. First of all, to find the expression for $\tilde{G}$, one needs to solve the homogeneous equation[23]

$$[(\hat{\Omega}_r/w)^\alpha + \hat{L}_D]\tilde{g} = 0 \quad \text{where } \tilde{g} = \tilde{M}_r\tilde{G} \tag{4.19}$$

Fortunately, this can be done within the approach called sudden perturbation approximation.[23,24] The details of the method can be found elsewhere.[23] Here, we will only outline its main points. In this approach, in the lowest order in the small parameter $\zeta = (\omega_{a,b}/w)(\alpha\lambda)^{-2} \ll 1$, the solutions $\tilde{g}(r)$ can be found by matching (at some distance r_0) two simplified solutions $\tilde{g}_-(r)$ and $\tilde{g}_+(r)$ obtained at $r < r_0$ and $r > r_0$, respectively. The functions $\tilde{g}_-(r)$ and $\tilde{g}_+(r)$ are still the solutions of eq 4.19 but with $\hat{\Omega}_r = \hat{\Omega}_r^{\ +} = \hat{J}_r$ and $\hat{\Omega}_r = \hat{\Omega}_r^{\ -} = \epsilon + \hat{K}_r + i\hat{H}_z^{\ 0}$, respectively. Since the matrixes $\hat{\Omega}_r^{\ +}$ and $\hat{\Omega}_r^{\ -}$ are diagonal in the bases independent of r, the problem of determining $\tilde{g}_-(r)$ and $\tilde{g}_+(r)$ reduces to solving one-channel equations. It is important to note that this piecewise solution $\tilde{g}(r)$, obtained in the lowest order of expansion in the powers of $\zeta \ll 1$, is independent of the auxiliary parameter r_0 (as was rigorously shown[23] and as actually should be).

The one-channel solutions required for constructing the matrix solutions $\tilde{g}_-(r)$ and $\tilde{g}_+(r)$ can be found analytically in a number of realistic models. To illustrate the most interesting specific features of spin effects, it is sufficient to consider the simplest ones. In our analysis, we will concentrate on the models of free diffusion and diffusion in a deep well u_r (called a cage model[24]).

Free Diffusion Model. For the free diffusion model (with $\hat{L}_D = -\lambda^2 r^{-2}\nabla_r(r^2\nabla_r)$), a direct comparison of the anomalous SLE (eq 4.18) with the corresponding conventional one[23] and the analysis made above (see section IVB2) allow for the conclusion that expressions for the values of spin effects derived earlier[23] remain the same but with the exchange and intraradical interaction terms $iJ_0e^{-\alpha_{ex}(r-d)}$ and iQ/D replaced by $[iJ_0e^{-\alpha_{ex}(r-d)}]^\alpha$ and $(iQ/D)^\alpha$, respectively. This observation enables one to obtain formulas for the values of MARY (Y_r), RYDMR [$Y_r(\omega)$], and CIDEP (Y_e) easily.

Cage Model. In the presence of the large deep potential well $u_r = -u_0\theta(R - r)$, for which $R \gg d$ and $u_0 \gg 1$, fast subdiffusion leads to rapid relaxation of the initial spatial distribution of the radical (created within the well) during the time $\tau_D = (R/\lambda)^{2/\alpha}/w$ and formation of the nearly homogeneous quasi-equilibrium state (cage) within the well. At $t > \tau_D$, reaction (with the second radical at $\mathbf{r} = 0$) and dissociation result in the quasi-stationary decay of the cage which is independent of the distance r_i of radical pair creation. In this system, the (anomalous) recombination kinetics can be found within the approach proposed in ref 24

$$Y_\nu = Tr\{\hat{l}_\nu[\hat{l} + (i\hat{H}_z^{\ 0}/w)^\alpha]^{-1}P_s\} \quad (\nu = r, e) \tag{4.20}$$

where $P_s = |S\rangle\langle S|$ is the projection operator on the $|S\rangle$ state and $\hat{l} = \hat{l}_r + \hat{l}_j + \hat{l}_e$. In eq 4.20, the supermatrixes $\hat{l}_r$, $\hat{l}_e$, and $\hat{l}_j$ describe the effect of recombination, escaping from the cage, and exchange interaction, respectively

$$\hat{l}_r = (3d\lambda^2/R^3)\hat{\phi}_S(1 + \hat{\phi}_S)^{-1}$$
$$\hat{l}_e = 3(\lambda/R)^2 e^{-u_0} \tag{4.21}$$

and $\hat{l}_j = (3\lambda^2/R^3)[L_j|ST_0\rangle\langle ST_0| + L_j^*|T_0S\rangle\langle T_0S|]$, where $L_j = \alpha_j^{-1}\{d\alpha_j + \ln[2J_0/(w\lambda^2\alpha_j^2)] + i\pi/2\}$, with $\alpha_j = \alpha\alpha_{ex}$ and $\hat{\phi}_S = (\Delta d/\lambda^2)(k_0\hat{\kappa}_S/w)^\alpha$.

Noteworthy is that, in accordance with the general properties of the subdiffusion-assisted processes and the corresponding non-Markovian SLEs mentioned above, the general expression 4.20 for anomalous observables differs from the conventional one[24] by replacing $\hat{H}_z^0$ by $(\hat{H}_z^0)^\alpha$ and renormalizing the reaction and relaxation radii.

3. Results. A simple inspection of general matrix formulas of section IVB2 demonstrates that the expressions for the amplitudes of anomalous and conventional spin effects are actually very similar. As we have already mentioned above, the difference mainly reduces to replacing the conventional reaction and dephasing radii by the corresponding anomalous ones and changing the spin Hamiltonian $\hat{H}_z$ with $(\hat{H}_z)^\alpha$. The last change shows itself in the change of the dependence of spin effects on the ST_0 splitting

$$Q = \omega_a - \omega_b \tag{4.22}$$

For example, in the conventional free diffusion model spin effects are $\sim|Q|^{1/2}$, while in the anomalous free diffusion (subdiffusion) one spin effects are $\sim|Q|^{\alpha/2}$ (see below).

MARY. In the considered limit of the strong magnetic field B, $B \gg A_j^\mu/(g_\mu\beta_B)$, the effect of spin evolution on the reaction yield called MARY can be studied within the ST_0 approximation,[4] which takes into account that for strong B the contribution of $|T_\pm\rangle$ terms to the reaction yield is negligibly small and the spin Hamiltonian is given by eq 4.10 with $\omega_1 = 0$ and $\omega = 0$. We also put $J_0 = 0$ because the effect of the exchange interaction on MARY is known to be negligibly weak.[2]

1. Free Diffusion Model. Taking into account the expression for the yield Y_r in the case of conventional diffusion[23] and above remarks on the relation between this formula in conventional and anomalous processes, one can write in the limit of strong reactivity in the S state and initial population of the T_0 state

$$Y_r = (d/r_i)\phi_r[1 + (ReL_j/d - 1/2)\phi_r]^{-1} \tag{4.23}$$

where $\phi_r = \cos(\pi\alpha/4)(|Q|d^2/\lambda^2 w)^{\alpha/2}$. Noteworthy is the anomalously weak dependence of Y_r on the parameter $|Q|d^2/\lambda^2 w$ for $\alpha < 1$, which reduces to the conventional one at $\alpha = 1$.

2. Cage Model. The important features of anomalous MARY dependencies can be demonstrated in the limit of weak magnetic interactions, $(|Q|/w)^\alpha \ll l_e,|\hat{l}_r|$, in which one can evaluate MARY with the lowest order of expansion of Y_r (eq 4.20) in the powers of $\hat{H}_z^0$

$$Y_r \approx (l_s/l_0) - (l_s/l_0^2)Tr[P_S(i\hat{H}_z^0/w)^\alpha P_S] \tag{4.24}$$

where $l_s = Tr(P_s\hat{l}_rP_s)$ is the reactivity in the singlet state and $l_0 = l_s + l_e$. A straightforward evaluation with the use of eq 4.24 gives the expression

$$Y_r = l_s l_0^{-1} - \frac{1}{4} l_s l_0^{-2} \cos\left(\frac{\pi}{2}\alpha\right)(|Q|/w)^\alpha \tag{4.25}$$

The nonanalytical dependence $Y_r \sim |Q|^\alpha$ is just a manifestation of the anomalous nature of subdiffusion in the well. Noteworthy is that in the case where $\alpha \to 1$ the $\delta\omega$-dependent part vanishes, because in eq 4.24 the spin-dependent contribution to Y_r is taken into account in the lowest order in H_z^0 $[\sim(H_z^0)^\alpha]$. At $\alpha = 1$, however, this term (linear in H_z) does not contribute to Y_r.

CIDEP. Following the above-mentioned relation between formulas for spin effects in processes assisted by conventional and anomalous diffusion, one can relatively easily obtain the expression for anomalous CIDEP using the conventional one.[23]

1. Free Diffusion Model. In the case of anomalous diffusion (similar to eq 4.23)

$$Y_e = \pi(2\alpha\alpha_{ex})^{-1}\tan(\pi\alpha/4)Y_r(d/r_i = 1) \tag{4.26}$$

Noteworthy is that for subdiffusion-assisted radical pair recombination ($0 < \alpha < 1$) the CIDEP value Y_e only weakly depends on α.

2. Cage Model. In the cage model, CIDEP can be estimated by means of the general expression 4.20. As in the case of MARY, we will restrict ourselves to the limit of weak magnetic interactions, $(|Q|/w)^\alpha \ll l_e,|\hat{l}_r|$, and will evaluate CIDEP in the lowest order of expansion of Y_e in powers of $\hat{H}_z^0$

$$Y_e \sim \frac{\pi}{2}(\alpha\alpha_{ex})^{-1}(l_e/l_0^2)\sin\left(\frac{\pi}{2}\alpha\right)(|Q|/w)^\alpha \tag{4.27}$$

This formula shows that the power-type dependence $Y_e(Q)$ is similar to $Y_r(Q)$ and differs from that predicted by the free diffusion model (see eq 4.26) in the two times larger exponent of the power dependence. Note that for $\alpha = 1$ formula 4.27 describes the case of conventional caging.[24]

RYDMR. For definiteness and brevity, we will analyze specific features of RYDMR within the cage model. The case of free diffusion differs only in the value of the exponent of the characteristic power-type dependencies (see below).

Consideration of the most important specific features of RYDMR can significantly be simplified in the limit of large ST_0 coupling $\omega_{ST0} \equiv Q = \omega_a - \omega_b \sim \langle A^\mu\rangle$ (see eq 4.10) and the relatively weak microwave field ω_1: $(|Q|/w)^\alpha \gg |l_r|$, l_e and $(\omega_1/w)^\alpha \lesssim |l_r|$, l_e. In this limit, quantum coherence effects on the evolution of all states with large splitting ($\sim Q$) are negligible[24] and evolution can be treated with balance equations.

Coherence effects are important only for four nearly degenerate pairs of states describing resonances, which do not overlap in the considered limit. These pairs can be combined into two groups, $(|\pm\rangle_b|\mp\rangle_a, |T_\pm\rangle)$ and $(|\pm\rangle_a|\mp\rangle_b, |T_\pm\rangle)$, denoted hereafter as $a_\pm$ and $b_\pm$, respectively. Transitions in pairs $\mu_\pm$ ($\mu = a, b$) are associated with those in the corresponding separate radical μ.

The states $|\pm\rangle_a|\mp\rangle_b$, corresponding to the zeroth z-projection of the total spin ($S_z = 0$), are the same for systems $\mu = a$ and $\mu = b$. However, these systems can be considered as uncoupled because in the studied limit of large $|Q|$ values efficient transitions in systems a and b occur at different values of ω (i.e., corresponding resonances do not overlap). For this reason, it is possible to distinguish the same states $|\pm\rangle_a|\mp\rangle_b$, belonging to a and b systems, and denote them as $|a\rangle$ or $|b\rangle$, respectively (the subscript $\pm$ or $-$ can be omitted as it will be explained below). The initial $|S\rangle$ state of the radical pair corresponds to the population of $|a\rangle$ and $|b\rangle$ states with a probability of 1/2.

Notice that these states are reactive with reactivity matrices $\hat{l}_r^\mu$ similar for all systems and determined as the two-level variant of formula 4.21. The matrices $\hat{l}_r^\mu$ describe reaction with the rate approximately equal to $l_s/2$, where $l_s = Tr(P_s\hat{l}_rP_s)$ is the reactivity in the $|S\rangle$ state.

All pairs give the same contribution to the total yield Y_r, differing only in the resonance frequency (ω_a or ω_b) if they correspond to different radicals. Therefore, we can combine the identical contributions of the pairs μ_+ and μ_- into one Y_μ of two times larger magnitude and omit subscripts $+$ and $-$ in the notation of the pairs and their parameters, as it has been mentioned above. In doing so, we arrive at the representation of Y_r in the form

$$Y_r = Y_a + Y_b \qquad (4.28)$$

where Y_μ ($\mu = a, b$) are given by

$$Y_\mu = Tr\{P_\mu \hat{l}_r^\mu [\hat{l}_r^\mu + l_d + (i\hat{H}_\mu/w)^\alpha]^{-1} P_\mu\} \qquad (4.29)$$

with $P_\mu = |\mu\rangle\langle\mu|$ and $\hat{l}_r^\mu \approx (1/2)l_s\{P_\mu, ...\}$.

In the considered limit of weak microwave field ω_1, the effects of ω_1-induced transitions can be treated perturbatively in the lowest order expansion of Y_r in $|(\hat{H}_\mu/w)^\alpha/|\hat{l}_{r,e}| \ll 1$. In this approximation

$$Y_\mu \approx \frac{1}{2}(l_s/l_\mu) - \frac{1}{2}(l_s/l_\mu{}^2) Tr[P_\mu (i\hat{H}_\mu/w)^\alpha P_\mu] \qquad (4.30)$$

in which $l_s = Tr(P_s \hat{l}_r P_s)$ and $l_\mu \approx (1/2)l_s + l_d$.

A calculation using eq 4.29 gives for the magnetic-field-dependent part y_r, which is called the RYDMR spectrum

$$y_r(\omega) = y_a(\omega - \omega_a) + y_b(\omega - \omega_b) \qquad (4.31)$$

where y_μ ($\mu = a, b$) is written as

$$y_\mu(z) = -\frac{1}{2}(l_s/l_\mu)^2 Tr[P_\mu (i\hat{H}_\mu/w)^\alpha P_\mu] \qquad (4.32)$$

$$= -\frac{1}{2}\cos\left(\frac{1}{2}\pi\alpha\right)(l_s/l_\mu)^2 \xi_1{}^\alpha (1 + z^2)^{\alpha/2-1} \qquad (4.33)$$

where $z = \omega/\omega_1$ and $\xi_1 = \omega_1/w$.

It is worth noting some important specific features of the anomalous RYDMR spectrum predicted by eq 4.33:

(1) Unlike Markovian diffusion, subdiffusion leads to the nonanalytical dependence of the spectrum on H_μ which can be obtained in the lowest order in H_μ. Similar to MARY, the lowest order value of RYDMR vanishes in the limit $\alpha \to 1$, because at $\alpha = 1$, the RYDMR amplitude is determined by the next term of expansion in H_μ.

(2) At large ω (at line wings) values, the RYDMR spectrum contributions $y_\mu(\omega)$ ($\mu = a, b$) decrease as $y_\mu(\omega) \sim 1/\omega^{2-\alpha}$, that is, remarkably slower than the Lorenzian $y(\omega) \sim 1/\omega^2$. This slower behavior can be used for identification and analysis of subdiffusive motion.

(3) The width of resonances is determined by the microwave field strength ω_1. This means that RYDMR spectra are always measured in the saturation regime.[1]

(4) The dependence of the anomalous signal amplitude Y_r on the microwave field strength ω_1 is nonanalytical, unlike that for conventional diffusion ($\sim\omega_1{}^2$). This anomalous Y_r dependence on ω_1 can also be used for the analysis of subdiffusion.

(5) At first sight, the saturation regime is a manifestation of long memory effects on the processes governed by subdiffusion and the absence of the characteristic decay time. Therefore, in the presence of such time, resulting, for example, from spin-independent decay of radicals, the width seems to depend on this time. In reality, however, this is not true. Indeed, in the presence of decay with the rate w_0, the magnetic-field-dependent yield contributions y_μ ($\mu = a, b$) are still given by eq 4.32 but with $(i\hat{H}_\mu/w)^\alpha$ replaced by $[(w_0 + i\hat{H}_\mu)/w]^\alpha - (w_0/w)^\alpha$

$$y_\mu(z) \sim (1 + z^2)^{-1}[Re(1 + i\xi_1{}^0\sqrt{1 + z^2})^\alpha - 1] \qquad (4.34)$$

where $z = \omega/\omega_1$ and $\xi_1{}^0 = \omega_1/w_0$. It is easily seen that in the limit $\omega_1 \gg w_0$ this expression reproduces eq 4.33, while in the opposite limit it predicts $y_\mu(z) \sim 1/(1 + z^2)^{1-\alpha}$. Therefore, the characteristic relaxation time does not show itself in the change of the line width of RYDMR spectra, only slightly changing the line shape.

Note that, similar to other magnetic field effects discussed above, in the free diffusion model formula for the RYDMR spectrum, $Y_r(z)$ differs from eq 4.34 only in the two times smaller value of the exponent ($\alpha/2$) of the power-type dependence.

V. Concluding Remarks

This work concerns the study of the specific features of spin relaxation and spin effects in radical pairs undergoing anomalous (of type of subdiffusion) relative motion. The work concentrated on the analysis of (1) the ESR spectrum of biradicals in the limit of short effective (correlation) time of orientational relaxation and (2) magnetic field (spin) effects in subdiffusion-assisted radical pair recombination. The analysis was made with the use of the non-Markovian SLE derived within the CTRW approach which proved to be quite efficient in analyzing considered multilevel quantum (spin) systems.

Some subtle properties of spectral and kinetic characteristics of the above-mentioned processes were found: the peculiarities of ESR line shape of biradicals and its dependence on the parameters of processes, spin effect generation rates, RYDMR line shape, etc. Analysis of these peculiarities allows one to clarify the specific features of anomalous stochastic motion of particles in some disordered nonequilibrium media. In particular, the anomalous spectrum of biradicals, unlike conventional spectrum, possesses quite pronounced shoulders in the wide region of mobilities as well as distinguishable singularities at some frequencies.

It is important to note that the majority of specific features considered above are determined by the only anomaly parameter $\alpha < 1$. To clarify this fact, it is worth adding some comments.

(1) In the case of anomalous stochastic reorientation, α governs the long time behavior of the orientation correlation function $P(t) \sim (wt)^{-\alpha}$. The slow decay of $P(t)$ alone results in the above-discussed peculiar behavior of the reorientation-induced relaxation in quantum systems in the limit of short time w^{-1}. As applied to dephasing and the spectrum line shape, instead of the conventional narrowing and δ-function-like spectrum, we obtained a very nontrivial quite broad line shape independent of w.

(2) As for anomalous diffusion (subdiffusion), the parameter α controls a similar long time decay of the memory in the kinetics of diffusion jumps, $P(t) \sim (wt)^{-\alpha}$, which manifests itself in the anomalous long time dependence of the mean square displacement $\langle r^2\rangle \sim t^\alpha$. This strong change of the migration kinetics results in that of the statistics of subdiffusive reencounters and subdiffusion-assisted radical pair recombination kinetics, for example, the recombination yield $Y_r \sim 1/(wt)^{1+\alpha/2}$.[23] The change of the reencounter statistics leads, in turn, to the anomalous characteristic dependencies of spin effect amplitudes on the magnetic parameters with a major part of these dependencies controlled by the only parameter α. Moreover, the most simple predictions of our rigorous consideration can be reproduced by the first reencounter approximation[3] with the anomalous reencounter probability $\sim Y_r(t)$. The characteristic time parameter w^{-1} (the time of the onset of the asymptotic behavior of $P(t)$) determines only the amplitudes of the majority of observables rather than their dependencies on physically interesting parameters, as in the case of line shapes, dependence of spin effects on interaction Q, microwave field ω_1, etc.

Noteworthy is that the found dependence of observables on the only parameter simplifies the possible observation and analysis of anomalous effects and allows us to obtain α from the experimental results.

Concerning the experimental investigations of spin effects, they are usually made in connection with the analysis of mechanisms of chemical processes of paramagnetic particles. Typically, the processes under study include a few reactions and are described by the complicated schemes with quite a large number of adjustable parameters. In such a case, the manifestation of the details of relative motion is significantly shaded by other effects. Unfortunately, only in very few works spin effects are observed in pure model systems and are used for the analysis of the nature and specific features of the relative motion of particles. A number of them are summarized in reviews.[3,4] Some recent results have been presented in ref 25.

In this work, we restricted ourselves to analytical analysis of the processes, however, the proposed method also allows for the important simplification of numerical treatment of the processes, especially in much more complicated multilevel spin systems: pairs of triplet excited molecules, magnetic clusters, magnetic glasses, and so forth, by reducing the problem to operations with simple Hamiltonian matrices.

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