

# Current state of the spin exchange theory in dilute solutions of paramagnetic particles. New paradigm of spin exchange and its manifestations in EPR spectroscopy

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## Contents

<b>1. Introduction</b>	<b>951</b>
<b>2. Calculations of the bimolecular spin exchange rate constant</b>	<b>953</b>
2.1 Mutual spin flip for particles with the spin $S = 1/2$ ; 2.2 Kinetic equations for the spin density matrix in the model of sudden collisions of particles; 2.3 Calculations of the spin exchange rate constant in the approximation of instantaneously switched exchange interaction; 2.4 Kinetic equations for the bimolecular spin exchange taking the extended nature of exchange interaction into account; 2.5 Calculations of the effective spin exchange radius for arbitrary-spin particles with the extended nature of the exchange interaction and the diffusive propagation of particles through the interaction region taken into account; 2.6 Spin exchange between charged particles with the spin $S = 1/2$ in electrolytes	
<b>3. Paramagnetic relaxation caused by the spin–spin dipole–dipole interaction of paramagnetic particles in liquids</b>	<b>963</b>
3.1 Spin Hamiltonian of the dipole–dipole interaction of paramagnetic particles; 3.2 Kinetic equations describing the electron paramagnetic relaxation in liquids caused by the dipole–dipole interaction; 3.3 Kinetic equations for typical EPR experiments	
<b>4. Manifestation of the spin exchange and dipole–dipole interaction in the shape of EPR spectra of free radicals</b>	<b>966</b>
4.1 General solution for the shape of EPR spectra for radicals in solutions; 4.2 New look at the role of spin coherence transfer. Collective evolution modes of the system spin coherence; 4.3 Collective motion modes of spin coherence for model systems	
<b>5. How can the spin exchange rate be extracted from EPR spectra?</b>	<b>971</b>
5.1 General observations; 5.2 Method for determining the spin exchange rate constant from EPR spectra	
<b>6. Prospects for using the spin exchange</b>	<b>973</b>
<b>7. Conclusions. Shift in the spin exchange paradigm</b>	<b>974</b>
<b>References</b>	<b>974</b>

**Abstract.** Kinetic equations are presented for single-particle spin-density matrices with the Heisenberg exchange interaction in bimolecular collisions of particles and the dipole–dipole spin–spin interaction between particles taken into account. It is shown that interactions between individual paramagnetic particles, despite being rather weak compared to the exchange interaction, can result in a nonequivalent spin exchange. Spin-coherence transfer generates collective modes of quantum spin coherence motion. Collective resonance lines have a mixed form (absorption + dispersion). A new interpretation of the exchange narrowing of the spectrum when the spin-coherence transfer rate is sufficiently large is proposed. An advanced

theory of paramagnetic relaxation of paramagnetic particles in dilute solutions due to dipole–dipole interaction is discussed. A modern paradigm of spin exchange is also presented.

**Keywords:** spin probes, exchange and dipole–dipole interaction, spin-exchange rate constant, decoherence of spin, spin coherence transfer, EPR spectrum shape, mixed form of spectral line (absorption + dispersion), exchange narrowing of spectra

## 1. Introduction

Spin exchange is changes in the spin state of unpaired electrons caused by the exchange interaction in bimolecular collisions of paramagnetic particles. In collisions of paramagnetic particles, the electron wave functions overlap and the electron energy depends on the total electron spin of colliding particles. The dependence of the energy on the spin multiplicity can be described by adding an exchange interaction term [1, 2]

$$V_{\text{ex}} = \hbar J(r_{12}) \mathbf{S}_1 \mathbf{S}_2 \quad (1)$$

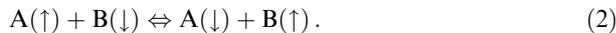
to the Hamiltonian. Here,  $J$  is the exchange integral in circular frequency units,  $r_{12}$  is the distance between colliding particles,

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and  $S_{1,2}$  are the operators of their spin moments measured in  $\hbar$  units. For particles with the spin  $S = 1/2$ , the elementary spin exchange event can be the mutual spin flip in two particles A and B,



The arrows indicate the two possible orientations of the electron spin moment with respect to the quantization axis. We call elementary event (2) the equivalent spin exchange. Possible changes in the spin states in collisions of particles A and B do not reduce to only such an equivalent spin exchange: in collisions, along with the exchange interaction, spin interactions of individual particles, such as the hyperfine interaction of electrons with magnetic nuclei, are also manifested.

We assume that the splitting of spin levels of individual particles can be described by a parameter  $\Delta$ . Then, obviously, the necessary condition for realizing the equivalent spin exchange is the relation

$$|J| \gg |\Delta|. \quad (3)$$

But this condition is not sufficient. To ignore the splitting of spin levels of individual particles in spin-exchange efficiency calculations, another condition,

$$|\Delta|\tau_c < 1, \quad (4)$$

must also be satisfied, where  $\tau_c$  is the collision time. If conditions (3) and (4) are not satisfied, the exchange interaction in bimolecular collisions should be expected to not result in spin exchange in the sense of an equivalent exchange. However, the term ‘spin exchange’ is also used in a broader sense, meaning any changes in the spin states of colliding particles, even if the exchange interaction ‘interferes’ with other spin-dependent interactions of particles. When the condition

$$|J|\tau_c > 1 \quad \text{or} \quad |J|\tau_c < 1 \quad (5)$$

is satisfied, the exchange interaction is respectively called strong or weak.

The rate of bimolecular collisions in a condensed phase was first calculated by Smoluchowski [3], who obtained the well-known expression

$$Z_{A0} = 4\pi(r_A + r_B)(D_A + D_B)C_B \equiv K_D C_B \quad (6)$$

for the collision rate of a separate type-A molecule with type-B molecules, where  $K_D \equiv 4\pi b D_{AB}$ . Here,  $r_A$  and  $r_B$  are the radii of spheres representing molecules,  $C_B$  is the concentration of molecules B, and  $D_A$  and  $D_B$  are the diffusion coefficients of molecules A and B,  $D_{AB} = D_A + D_B$ ,  $b = r_A + r_B$  is the distance of closest approach of spheres, called the collision radius, and  $K_D$  is the rate constant of bimolecular collisions, which is referred to as a constant in the sense of being independent of the concentration of particles. We note that when the concentration is measured as the number of spins per  $\text{cm}^3$ , the dimension of  $K_D$  is  $[\text{cm}^3 \text{ s}^{-1}]$ .

In a condensed medium, the same pair of molecules collides many times, as is experimentally shown in [4]. Two molecules in the same pair collide repeatedly. Taking such repeated collisions in the same pair of particles in a condensed medium into account, we can speak about bimolecular

encounters, including the first and all repeated collisions in a chosen pair of molecules. The statistics of repeated collisions are discussed in detail in books [5, 6]. Smoluchowski formula (6) gives the rate of first collisions. For charged molecules (spheres), Debye [7] obtained an analog of (6),

$$Z_{A0} = 4\pi r_{\text{eff}} D_{AB} C_B, \quad r_{\text{eff}} = f_D b, \quad (7)$$

with the parameter  $f_D > 1$  for charged molecules with different signs and  $f_D < 1$  for charged molecules with the same sign [7, 8].

Bimolecular processes are characterized by a quantity assigned to the unit concentration of molecules, which is called the rate constant of the process. In the case of spin exchange, the rate constant can be written in the form

$$K_{\text{ex}} = 4\pi r_{\text{ex}} D_{AB}. \quad (8)$$

The effective radius  $r_{\text{ex}}$  depends on the interaction between molecules. However,  $r_{\text{ex}}$  also accumulates the effect of repeated collisions, affecting the total time during which a pair of interacting spins is located in the interaction region. We show below that the result of the encounter can also depend on the spin dynamics of particles in time intervals between repeated collisions.

An important aspect of the spin exchange theory is the manifestation of spin exchange in electron paramagnetic resonance (EPR) spectroscopy. The first theoretical interpretation of changes in spectral shapes observed in EPR experiments was given in [9]. The shape of the spectrum was described by adding terms to the equation of motion for the magnetization of paramagnetic particles [9], as is done in chemical kinetics:

$$\begin{aligned} \left(\frac{\partial \mathbf{M}_A}{\partial t}\right)_{\text{ex}} &= -K_{\text{ex}} C_B \mathbf{M}_A + K_{\text{ex}} C_A \mathbf{M}_B, \\ \left(\frac{\partial \mathbf{M}_B}{\partial t}\right)_{\text{ex}} &= K_{\text{ex}} C_B \mathbf{M}_A - K_{\text{ex}} C_A \mathbf{M}_B. \end{aligned} \quad (9)$$

Here,  $\mathbf{M}_A$  and  $\mathbf{M}_B$  are the total magnetization vectors for spins A and B.

The EPR spectra calculated taking the spin exchange into account as in (9) reproduce the characteristic spectral transformations upon increasing the spin concentration. Namely, in the case of a slow exchange, spectral lines broaden and shift to the center of gravity. As the spin exchange rate increases, exchange spectral narrowing begins. The broadening of spectral lines in the region of a relatively slow spin exchange can be interpreted using the uncertainty relation. The spin exchange changes the spin state and therefore shortens the spin lifetime in a specified state, thereby leading to the ‘spread’ of spin energy levels. The spectral narrowing is explained by the effect of averaging the interactions of paramagnetic particles by rapid spin exchange, which results in splitting their EPR spectra. However, the situation proves to be more complicated [10].

Moreover, apart from the exchange interaction, there is the dipole–dipole spin–spin interaction of paramagnetic particles resulting in a dependence of the shape of EPR spectra on the concentration of paramagnetic particles. Thus, the separation of contributions from the bimolecular spin exchange process and dipole–dipole interaction is an urgent problem. Because of this, we also briefly consider the state-of-the-art theory of paramagnetic spin relaxation in

nonviscous liquids caused by dipole–dipole interaction. Considerable attention is devoted to a new paradigm of EPR spectrum shape transformations caused by spin exchange and dipole–dipole interaction [10, 11].

In our books [12, 13] published forty years ago, we presented a comprehensive review of spin exchange investigations and applications at that time. These books were received well by the world’s scientific community and facilitated the development of the spin probe method and its applications in chemistry, molecular biology, and medicine. However, theoretical results confirmed by experiments have been accumulated since then that fundamentally change our concepts about the motion of spins of unpaired electrons in paramagnetic particles in diluted solutions. In fact, the paradigm of spin exchange and its manifestation in EPR spectroscopy has changed.

The shift of the resonance spin frequency related to the spin dynamics during bimolecular collisions (directly in collisions and between them in the same pair of colliding particles) was theoretically predicted in [14]. This frequency shift was experimentally confirmed and thoroughly investigated (see, e.g., [15–18]). The spin exchange rate constant was first consistently calculated in [19] for charged paramagnetic particles with spin  $1/2$ . The spin exchange rate constants were carefully measured for nitroxyl free radicals [19, 20]. It was demonstrated in a number of papers (see, e.g., [10, 11, 17, 18, 21, 22]) that due to the spin exchange, the individual spectral lines have a mixed shape, being the sum of symmetric and antisymmetric functions (see, e.g., [10, 11, 17, 18]). The influence that the anisotropic distribution of the spin density on the ‘surface’ of paramagnetic particles has on the spin exchange rate was first experimentally studied in [23].

Spin exchange studies should always take into account that along with the exchange interaction, the dipole–dipole spin–spin interaction also exists, whose contribution to the spin dynamics depends on the spin concentration. The contribution of the dipole–dipole interaction to spin decoherence was reconsidered in recent years [21, 22, 24]. It was shown that unlike the exchange interaction, the dipole–dipole interaction tends not to shift spectral lines to their center of gravity, but ‘pushes them apart’. This feature of the dipole–dipole interaction contribution to spin decoherence has been confirmed experimentally [18]. For uncharged particles with arbitrary spins, the spin exchange rate constant was calculated for the diffusion propagation of particles through the region of the extended exchange interaction [25]. These studies resulted in the formulation of a new paradigm for measuring the spin exchange rate from analysis of EPR spectra in the linear response region (see, e.g., [10, 11]).

The aim of this review is to present a complete state-of-the-art theory of the bimolecular spin exchange and its manifestations in EPR spectra. Of special interest for experimentalists should be Section 5, presenting the modern protocol for measuring the spin exchange rate constant from an analysis of the EPR spectrum shape.

## 2. Calculations of the bimolecular spin exchange rate constant

The model of a sudden switching on the exchange interaction, being the simplest of possible bimolecular spin exchange models in solutions, is most often used to calculate the spin exchange rate constant and interpret spin exchange experimental data. Here, we consider the results of the bimolecular

spin exchange theory obtained in this model of colliding particles.

It is assumed that particles collide with each other only once, the second collision being disregarded. In addition, it is assumed that the exchange interaction in a collision is switched on and off instantaneously [26, 27]. A mutual spin flip in colliding particles is regarded as an elementary spin exchange event (2). In this model, the effective spin exchange radius is

$$r_{\text{ex}} = p_{\text{ex}} b, \quad (10)$$

where  $p_{\text{ex}}$  is the spin exchange probability for one collision of a pair of molecules in solution. The effective spin exchange radius  $r_{\text{ex}}$  in this model should always be smaller than the collision radius of spheres, because the probability cannot exceed unity,  $p_{\text{ex}} \leq 1$ .

### 2.1 Mutual spin flip for particles with the spin $S = 1/2$

Most spin-exchange studies were performed with stable free radicals with the spin  $S = 1/2$ , because they are promising for applications as spin probes or spin labels. In this case, the probability of mutual spin flip (equivalent spin exchange) and the equivalent spin exchange rate constant are given by [26, 27]

$$p_{\text{ex}} = \frac{J^2 \tau_c^2 / 2}{1 + J^2 \tau_c^2}, \quad K_{\text{ex}} = p_{\text{ex}} K_D. \quad (11)$$

Here,  $J$  is the exchange integral value at the collision radius  $b$  in units [ $\text{rad s}^{-1}$ ] and  $\tau_c$  is the average residence time of an ensemble of colliding pairs of particles at the collision radius. According to (11),  $p_{\text{ex}} \leq 1/2$  in the sudden collision model. This means that the spin exchange rate constant at the collision radius  $b$  in this model must be not greater than half the rate constant of bimolecular collisions calculated by (6) for neutral molecules or (7) for charge molecules.

The result in (11) is obtained as follows [26]. The exchange interaction causes a mutual spin flip with the probability

$$p(t) = \sin^2 \frac{Jt}{2}. \quad (12)$$

It is assumed that the collision duration  $t$  in the ensemble of pairs has the Poisson distribution

$$\varphi(t) = \frac{1}{\tau_c} \exp\left(-\frac{t}{\tau_c}\right). \quad (13)$$

By averaging the mutual spin flip probability over the ensemble, we obtain (11).

Equation (11) estimates the spin exchange efficiency from below because it ignores repeated collisions of a pair of paramagnetic particles. Repeated collisions can be taken into account by assuming that the time  $\tau_c$  in (11) is equal to the total residence time of a pair of particles in the exchange interaction region for all collisions, the first and repeated, in this region. We assume that the exchange interaction is instantaneously switched off when the distance between two particles is in the narrow interval  $(b, b+a)$ ,  $a \ll b$ . In the continuous molecular diffusion model, the total residence time spent by both colliding particles during one collision in the configuration space between spheres with radii  $b$  and  $b+a$  has the form [5, 6]

$$\tau_{\text{cs}} = \frac{ba}{D_{\text{AB}}}. \quad (14)$$

We note that the use of expression (14) for the total residence time of two particles in the exchange interaction region to calculate efficiency  $p_{\text{ex}}$  (11) overstates it, because the decoherence of spins is ignored, which can occur between repeated collisions at the distance of the exchange interaction switching [21]. This means that  $\tau_{\text{cs}} > \tau_{\text{eff}} > \tau_{\text{c}}$ . The ‘thickness’  $a$  of interaction region (14) can be estimated as follows. The exchange integral for the intermolecular exchange interaction of paramagnetic particles can be assumed to be proportional to the squared modulus of the overlap integral of electron orbitals occupied by the unpaired electrons of interacting molecules [2]. Therefore, we can expect that the exchange integral is an exponentially decaying function,

$$J_{\text{AB}}(r) = J_{\text{AB}}(b) \exp[-\varkappa(r - b)], \quad (15)$$

where  $J_{\text{AB}}(b)$  is the exchange integral value at the atomic collision radius and the parameter  $\varkappa$  characterizes the exchange integral decay steepness with increasing the distance between interacting atoms. For interatomic interactions, the typical values are  $1/\varkappa \approx 0.03 - 0.1$  nm [28]. This value can be used to estimate the ‘thickness’  $a$  of the exchange interaction region:  $a \approx 1/\varkappa \approx 0.03 - 0.1$  nm. For free radicals, the exchange integral at a distance of the collision radius is estimated as  $J_{\text{AB}}(b) \sim 10^{12} - 10^{13}$  rad s<sup>-1</sup> [12, 13]. Using these estimates, we can see that for free radicals, the condition  $J(b)\tau_{\text{eff}} \gg 1$  is expected to hold. Then, according to (11),  $p_{\text{ex}} = 1/2$ , and the spin exchange rate constant is equal to half the rate constant of bimolecular collisions,  $K_{\text{ex}} = 2pbD_{\text{AB}}$ . However, the condition  $J(b)\tau_{\text{eff}} \gg 1$  means that for  $r > b$  the exchange integral can be rather large, and then the spin exchange rate should be calculated taking the extended nature of the exchange integral into account. Therefore, the real spin exchange rate constant can become equal to or even greater than the rate constant  $K_D$  of the first collision of spheres in (6). Theoretical calculations of the spin exchange rate constant taking the extended nature of the exchange integral into account are presented in Section 2.3.

## 2.2 Kinetic equations for the spin density matrix in the model of sudden collisions of particles

Consistent kinetic equations describing spin exchange processes in diluted solutions in the model of sudden collisions are derived in [29]. We consider a solution with paramagnetic particles A and B. According to [29], we divide spins into two subsystems: isolated paramagnetic particles and pairs of particles with the switched exchange interaction. Both subsystems are in dynamic equilibrium: for example, a certain paramagnetic particle A leaves the subsystem of paramagnetic spins with the rate  $K_D C_B$  ( $C_B$  is the spin concentration) and forms a pair AB, and pairs decompose at the rate  $\tau_{\text{c}}^{-1}$  into two isolated spins.

Before writing kinetic equations, we introduce the following notation. We let  $H_0(k)$  be the spin Hamiltonian of an isolated  $k$ th paramagnetic particle,  $V_{\text{ex}}$  the spin Hamiltonian of exchange interaction in the AB pair when particles are directly in contact at the collision radius (see (1)),  $\rho$  the spin density matrix, and  $\rho^{(2)}$  the spin density matrix of the AB pair. It is assumed that the density matrix of a pair during its formation is equal to the direct product of the spin density matrices of partners in the collision. It is shown in [30, 31] that kinetic equations

proposed in [29] can be written in the form (see, e.g., [12, Eqns (1.131)])

$$\begin{aligned} \frac{\partial \rho_{\text{A}}}{\partial t} &= -i\hbar^{-1}[H_{\text{A}}, \rho_{\text{A}}] \\ &\quad - K_D C_{\text{B}}(\rho_{\text{A}} - \text{Tr}_{\text{B}}\langle S(\tau)\rho_{\text{A}} \times \rho_{\text{B}}S^{-1}(\tau) \rangle), \\ \frac{\partial \rho_{\text{B}}}{\partial t} &= -i\hbar^{-1}[H_{\text{B}}, \rho_{\text{B}}] \\ &\quad - K_D C_{\text{A}}(\rho_{\text{B}} - \text{Tr}_{\text{A}}\langle S(\tau)\rho_{\text{A}} \times \rho_{\text{B}}S^{-1}(\tau) \rangle). \end{aligned} \quad (16)$$

In these equations, the collision matrix is introduced as

$$S(\tau) = \exp(-i\hbar^{-1}H\tau) \exp(i\hbar^{-1}H_0\tau), \quad (17)$$

where  $H_0 = H_{\text{A}} + H_{\text{B}}$  and  $H = H_0 + V_{\text{ex}}$ . The operator  $\text{Tr}_{\text{A(B)}}$  in Eqns (16) means contraction over spin variables A(B). The angular brackets denote averaging over the distribution of  $\tau$  in Eqn (13).

Kinetic equations (16) are written taking into account that there is a hierarchy of processes in time. There is an encounter of a given pair of molecules and encounters with new molecules. The characteristic time  $\tau_{\text{c}}$  of one encounter is considerably shorter than the diffusion mean free time, which can be estimated as  $1/(K_D C_{\text{A(B)}})$ . Kinetic equations (16) describe changes in single-particle spin density matrices at the mean free time scale. Therefore, we can perform averaging in (16) over a fast process at the scale  $\tau_{\text{c}}$ . In fact, both the left-hand side of (16) and the commutator term are mean values at the collision time scale. But the change in the single-particle matrix at the scale  $\tau_{\text{c}}$  can be disregarded. Therefore, only the term describing the spin dynamics during the collision is averaged in (16).

We note that kinetic equations for the exchange interaction of an extended nature and arbitrary interaction kinematics for the motion of two molecules are derived in Section 2.4. In the limit corresponding to the sudden interaction switching model, the general theory reproduces the theory based on this model.

Equations (16) can be represented in a more compact form by introducing the collision efficiency superoperator  $T = \langle S(\tau) \times S^{-1}(\tau) \rangle$ ,

$$T_{mn,kl} = \int \exp\left(-\frac{\tau}{\tau_{\text{c}}}\right) S_{mk}(\tau) S_{ln}^{-1}(\tau) \frac{d\tau}{\tau_{\text{c}}}. \quad (18)$$

As a result, Eqns (16) take the form

$$\begin{aligned} \frac{\partial \rho_{\text{A}}}{\partial t} &= -i\hbar^{-1}[H_{\text{A}}, \rho_{\text{A}}] - K_D C_{\text{B}}(\rho_{\text{A}} - \text{Tr}_{\text{B}}T\rho_{\text{A}} \times \rho_{\text{B}}), \\ \frac{\partial \rho_{\text{B}}}{\partial t} &= -i\hbar^{-1}[H_{\text{B}}, \rho_{\text{B}}] - K_D C_{\text{A}}(\rho_{\text{B}} - \text{Tr}_{\text{A}}T\rho_{\text{A}} \times \rho_{\text{B}}). \end{aligned} \quad (19)$$

The collision efficiency superoperator satisfies the equation [31]

$$[T, Q] = \Omega T - \frac{T - E}{\tau_{\text{c}}}, \quad (20)$$

where  $E$  is the unit operator and

$$\begin{aligned} Q_{mn,kl} &= -i\hbar^{-1}(H_{0mk}\delta_{nl} - H_{0ln}\delta_{mk}), \\ \Omega_{mn,kl} &= -i\hbar^{-1}(V_{mk}\delta_{nl} - V_{ln}\delta_{mk}). \end{aligned}$$

Introducing the matrices  $\sigma$  that describe small deviations of the spin system from thermodynamic equilibrium as

$$\rho_A = \rho_{0A} + \sigma_A, \quad \rho_B = \rho_{0B} + \sigma_B, \quad (21)$$

substituting (21) in (19), and keeping only terms linear in  $\sigma_A$  and  $\sigma_B$ , we obtain linear equations for the spin exchange kinetics when the system does not strongly deviate from equilibrium.

### 2.3 Calculations of the spin exchange rate constant in the approximation of instantaneously switched exchange interaction

**2.3.1 Spin exchange between particles with  $S = 1/2$ .** In the case of equivalent spin exchange, when only the exchange interaction  $S(\tau) = \exp(-i\hbar^{-1}V_{ex}\tau)$  is taken into account at the collision moment, Eqns (16) reproduce (11).

In this section, we present the results obtained for particles with the spin  $S = 1/2$  using kinetic equations (16)–(20) and taking the spin Hamiltonian of individual spins into account along with the exchange interaction. We assume that the spin Hamiltonians of particles A and B (see (17)) contain only the Zeeman energy of interaction with a constant magnetic field  $B_0$ , and the spins have different spectroscopic  $g$ -factors and therefore different Larmor frequencies (resonance in EPR experiments):

$$H_A = g_A \beta B_0 S_{Az} = \hbar \omega_A S_{Az}, \quad (22)$$

$$H_B = g_B \beta B_0 S_{Bz} = \hbar \omega_B S_{Bz}.$$

Here,  $\beta$  is the Bohr magneton and  $\omega_A$  and  $\omega_B$  are the Larmor frequencies of spins. The difference between spin frequencies can also be caused by the hyperfine interaction of unpaired electrons with magnetic nuclei. From Eqns (16)–(20), we obtain the linearized equations (for convenience, we let the eigenfunctions  $|+1/2\rangle$  and  $|-1/2\rangle$  of the operator  $S_z$  be denoted as  $\alpha$  and  $\beta$ ):

$$\begin{aligned} \frac{\partial \sigma_{A\alpha\alpha}}{\partial t} = & -K_{ex} C_B (\sigma_{A\alpha\alpha} \rho_{0B\beta\beta} - \sigma_{A\beta\beta} \rho_{0B\alpha\alpha}) \\ & + K_{ex} C_B (\sigma_{B\alpha\alpha} \rho_{0A\beta\beta} - \sigma_{B\beta\beta} \rho_{0A\alpha\alpha}), \end{aligned} \quad (23)$$

$$\frac{\partial \sigma_{A\alpha\beta}}{\partial t} = -i\omega_A \sigma_{A\alpha\beta} - W_1 \sigma_{A\alpha\beta} + W_2 \sigma_{B\alpha\beta},$$

where we set

$$\begin{aligned} K_{ex} = & \frac{J^2}{R^2} \left\langle \sin^2 \frac{Rt}{2} \right\rangle = \frac{1}{2} \frac{J^2 \tau_c^2}{1 + R^2 \tau_c^2}, \\ W_1 = & K_D C_B \left\{ 1 - \left\langle \exp \left[ \frac{i(\omega_A - \omega_B)t}{2} \right] \right. \right. \\ & \times \left[ \cos \frac{Rt}{2} - i \left( \frac{\omega_A - \omega_B}{R} \right) \sin \frac{Rt}{2} \right] \\ & \left. \left. \times \left[ \cos \frac{Jt}{2} - i \sin \frac{Jt}{2} (\rho_{0B\alpha\alpha} - \rho_{0B\beta\beta}) \right] \right\rangle \right\}, \quad (24) \\ W_2 = & K_D C_B \left\langle \frac{J}{R} \exp \left[ -\frac{i(\omega_A - \omega_B)t}{2} \right] \sin \frac{Rt}{2} \right. \\ & \left. \times \left[ \sin \frac{Jt}{2} + i \cos \frac{Jt}{2} (\rho_{0A\alpha\alpha} - \rho_{0A\beta\beta}) \right] \right\rangle, \\ R = & (J^2 + (\omega_A - \omega_B)^2)^{1/2}. \end{aligned}$$

A similar equation for spins B can be obtained by changing subscripts  $A \rightarrow B$ ,  $B \rightarrow A$  in (23) and (24). We note that in

the limit case  $J^2 \gg (\omega_A - \omega_B)^2$ ,  $R \approx J$ , the quantity  $K_{ex}$  in (23), (24) coincides with expression (11) obtained in [26, 27].

The angular brackets in Eqns (24) denote averaging over the distribution of collision durations (13). Kinetic coefficients  $W_1$  and  $W_2$  are complex in the general case. The real part of  $W_1$  describes the decoherence rate or the spin coherence relaxation caused by the exchange interaction in bimolecular collisions of paramagnetic particles. The imaginary part of  $W_1$  gives the spin frequency shift of  $\omega_A$ . The modulus of  $W_2$  characterizes the coherence transfer from spins B to spins A. The spin frequency shift caused by the exchange interaction in bimolecular collisions was theoretically studied in [14]. To demonstrate possible frequency shifts due to spin dynamics in collisions of particles, we consider two limit cases:

(1) the equivalent spin exchange,  $|J| > |\omega_A - \omega_B|$  and  $(\omega_A - \omega_B)\tau_c < 1$ ;

(2) the nonequivalent spin exchange,  $(\omega_A - \omega_B)\tau_c \gtrsim 1$ .

In the case of the equivalent spin exchange,  $W_1$  and  $W_2$  in (24) are considerably simplified:

$$\begin{aligned} W_1 \approx & K_D C_B \left[ \frac{1}{2} \frac{J^2 \tau_c^2}{1 + J^2 \tau_c^2} - i \frac{J \tau_c}{2(1 + J^2 \tau_c^2)} (\rho_{0B\alpha\alpha} - \rho_{0B\beta\beta}) \right], \\ W_2 \approx & K_D C_B \left[ \frac{1}{2} \frac{J^2 \tau_c^2}{1 + J^2 \tau_c^2} + i \frac{2}{4 + J^2 \tau_c^2} (\rho_{0A\alpha\alpha} - \rho_{0A\beta\beta}) \right]. \end{aligned} \quad (25)$$

It follows from Eqns (23) and (24) that the spin resonance frequency shifts as

$$\omega'_A = \omega_A - K_D C_B \frac{J \tau_c}{2(1 + J^2 \tau_c^2)} (\rho_{0B\beta\beta} - \rho_{0B\alpha\alpha}). \quad (26)$$

This shift can be called paramagnetic. The frequency shift of spins is obtained from (26) by interchanging subscripts A and B. The sign of the paramagnetic frequency shift depends on the exchange integral sign. The paramagnetic frequency shifts for both particles A and B have the same sign. This shift appears because spins are predominantly oriented in one direction, they produce some mean nonzero exchange interaction field at the location of their partners in the interaction (like the Weiss field in magnetic materials). Under usual conditions of spin exchange studies,  $\rho_{0B\beta\beta} - \rho_{0B\alpha\alpha} \sim 10^{-3}$ . Therefore, a frequency shift like (26) can be disregarded.

If the equilibrium dipole polarization of spins is negligibly small, then in the case of the equivalent spin exchange (cf. (11)),

$$W_1 = W_2 = K_{ex} C_B \frac{1}{2} \frac{J^2 \tau_c^2}{1 + J^2 \tau_c^2} K_D C_B. \quad (27)$$

For the nonequivalent spin exchange, the theory gives a result inconsistent with the result of a phenomenological theory [9]. Assuming that  $\rho_{0\alpha\alpha} - \rho_{0\beta\beta} = 0$ , we use (24) to obtain

$$\begin{aligned} W_1 = & p_{Aex} K_D C_B, \\ p_{Aex} = & \left\{ 1 - \left\langle \exp \left[ \frac{i(\omega_A - \omega_B)t}{2} \right] \right. \right. \\ & \left. \left. \times \left( \cos \frac{Rt}{2} - i \frac{\omega_A - \omega_B}{R} \sin \frac{Rt}{2} \right) \cos \frac{Jt}{2} \right\rangle \right\}, \\ W_2 = & p_{Bex} K_D C_B, \end{aligned} \quad (28)$$

$$p_{Bex} = \left\langle \frac{J}{R} \exp \left[ -\frac{i(\omega_A - \omega_B)t}{2} \right] \sin \frac{Rt}{2} \sin \frac{Jt}{2} \right\rangle.$$

The real part of  $p_{\text{Aex}}$  characterizes the decoherence efficiency of spins A caused by collisions with spins B.

Under the conditions  $(\omega_A - \omega_B)\tau_c < 1$ ,  $J^2 \gg (\omega_A - \omega_B)^2$ , and  $J^2\tau_c^2 \gg 1$ , the imaginary part of  $W_1$  gives the frequency shift of spin A. The frequency shift for spin B can be found similarly. As a result, we have

$$\begin{aligned}\Delta\omega_A &= -\frac{1}{4}(\omega_A - \omega_B)\tau_c K_D C_B, \\ \Delta\omega_B &= \frac{1}{4}(\omega_A - \omega_B)\tau_c K_D C_A.\end{aligned}\quad (29)$$

Thus, we see that the simultaneous influence of the exchange interaction and the difference between the resonance frequencies of colliding spins in a pair leads to the frequency shift of spins. We note that the resonance frequency shifts of spins A and B have opposite signs; moreover, the frequencies of A and B shift to the mean frequency. This result is expected. Indeed, it is well known that a sufficiently strong exchange interaction can lead to the exchange narrowing of an inhomogeneous EPR spectrum. The situation with frequency shifts can actually prove to be unexpected. A detailed analysis of Eqns (28) shows that the resonance frequency shift changes sign in the region  $|J|\tau_c \sim 1$  upon changing this parameter (the sign of  $\text{Im } p_{\text{Aex}}$  changes; see (28)).

The change of the frequency shift sign and the role of repeated collisions between particles are considered in [14]. It was shown there that the spin frequency shift increases due to repeated collisions. Repeated collisions can be qualitatively taken into account by assuming that  $\tau_c$  in Eqns (29) is the total duration of all collisions of two particles during one encounter in a solution (see (14)). However, the role of repeated collisions in the model of sudden exchange interaction switching, when colliding paramagnetic particles are in a narrow interval of collision radii ( $b, b+a$ ), cannot be taken into account only by replacing the duration of one collision by the total residence time of a pair of particles in the exchange interaction region during one encounter of this pair in solution. It was shown in [14] that an important role is played by the free precession of spins in intervals between repeated contacts when the exchange interaction is switched off. When the repeated collisions of a pair are taken into account, one more parameter,  $\tau_D = b^2/D_{\text{AB}}$ , appears. In the case of free radicals in nonviscous media, the conditions

$$|\omega_A - \omega_B|\tau_c < 1, \quad |\omega_A - \omega_B|\tau_D < 1 \quad (30)$$

are typically satisfied. Under these conditions, the resonance frequencies diverge when  $J\tau_c < 1$ :

$$\delta'_A \approx \frac{J^2\tau_c^2}{4} \left[ \delta\tau_c + \text{sign } \delta \left( \frac{|\delta|\tau_D}{2} \right)^{1/2} \right] K_D C_B, \quad (31)$$

$$\delta'_B \approx -\frac{J^2\tau_c^2}{4} \left[ \delta\tau_c + \text{sign } \delta \left( \frac{|\delta|\tau_D}{2} \right)^{1/2} \right] K_D C_A,$$

where  $\delta \equiv \omega_A - \omega_B$ . In another limit case  $J\tau_c > 1$ , the resonance frequencies converge (cf. (29)):

$$\delta'_A \approx -\frac{1}{4} \left[ \delta\tau_c + \text{sign } \delta \left( \frac{|\delta|\tau_D}{2} \right)^{1/2} \right] K_D C_B, \quad (32)$$

$$\delta'_B \approx \frac{1}{4} \left[ \delta\tau_c + \text{sign } \delta \left( \frac{|\delta|\tau_D}{2} \right)^{1/2} \right] K_D C_A.$$

The convergence of frequencies for  $J\tau_c > 1$  is expected, because a strong exchange interaction causes spectral narrowing, whereas the divergence of frequencies for  $J\tau_c < 1$  in Eqns (31) is unexpected.

The shift of resonance frequencies caused by the spin dynamics in collisions of particles was experimentally studied in [15–18] with the EPR spectra of nitroxyl radicals using interesting methodological procedures. For example, collisions between the same nitroxyl radicals were studied, but either  $^{14}\text{N}$  or  $^{15}\text{N}$  radicals were used in different experiments. In this situation, the exchange integral, the collision radius, and practically the diffusion coefficient and therefore the collision duration should coincide. These radicals differ only by hyperfine interaction constants (by  $\delta$  values in (31) and (32)) and the statistical weights of hyperfine-structure components in the EPR spectrum. But these quantities are known, which allowed verifying the correctness of theoretically predicted line shifts [17]. The additional spin frequency shift caused by spin evolution in collisions between particles predicted theoretically was verified in experiments with nitroxyl radicals with two equivalent  $^{14}\text{N}$  [16].

Thus, theoretical [14] and experimental [15–18] studies have shown that an important parameter for the spin exchange is  $q \equiv (\omega_A - \omega_B)\tau_c$ . Spin exchange experiments are usually performed under the conditions  $q < 1$  and  $J^2 > (\omega_A - \omega_B)^2$ . Because of this, the spin exchange theory was mainly developed just in this case of the equivalent spin exchange. In this situation, we have a good approximation according to (28):

$$p_{\text{Aex}} = p_{\text{Bex}} = \left\langle \frac{\sin^2 Jt}{2} \right\rangle = \frac{1}{2} \frac{J^2\tau_c^2}{1 + J^2\tau_c^2}.$$

The situation fundamentally changes if the condition  $q > 1$  holds. For example, for  $q > 1$  and  $J^2 > (\omega_A - \omega_B)^2$ , we have  $R \approx J$  and it then follows from Eqns (28) that

$$\begin{aligned}\text{Re } p_{\text{Aex}} &\approx 1 - \frac{1}{2} \frac{2 + J^2\tau_c^2 + q^2/4}{(1 + J^2\tau_c^2)(1 + q^2/4)}, \\ \text{Re } p_{\text{Bex}} &\approx \frac{1}{2} \frac{J^2\tau_c^2}{(1 + J^2\tau_c^2)(1 + q^2/4)}.\end{aligned}\quad (33)$$

Unlike the efficiency in the case of equivalent spin exchange (27), for quite large values of  $q$ , efficiencies (33) do not tend to the same value  $1/2$ . The limit values of efficiencies (33) are

$$\text{Re } p_{\text{Aex}} \rightarrow 1 - \frac{2}{4 + q^2} > \frac{1}{2}, \quad \text{Re } p_{\text{Bex}} \rightarrow \frac{2}{4 + q^2} < \frac{1}{2}. \quad (34)$$

We can see from (34) that for  $q \gg 1$ ,

$$\text{Re } p_{\text{Aex}} \rightarrow 1, \quad \text{Re } p_{\text{Bex}} \rightarrow 0. \quad (35)$$

Stable nitroxyl free radicals, for which the condition  $q < 1$  is typically satisfied, are often used as spin probes. Therefore, the spin exchange between nitroxyl radicals occurs in fact under conditions of the equivalent spin exchange, although a frequency shift was observed in experiments [15–18].

The nonequivalent spin exchange can be realized for triplet excitons [32] or in collisions among stable free radicals with paramagnetic complexes having very short paramagnetic relaxation times [33, 34].

We note that the earlier spin-exchange paradigm considered only the equivalent spin exchange. It was assumed

that only the exchange interaction can be taken into account at the collision moment. The modern paradigm includes both the equivalent and nonequivalent spin exchanges.

**2.3.2 Spin exchange between triplet excitons.** Rather interesting objects for studying spin exchange are the excited electron states with the total electron spin  $S = 1$ , triplet excitons (see, e.g., [35–37]). In the case of triplet excitons, a parameter  $D$  appears that characterizes the spin–spin interaction in isolated excitons. Due to this interaction, triplet excitons have two EPR frequencies, their difference being  $2D$ . The spin exchange between triplet excitons was theoretically analyzed in [32]. Spin-exchange characteristics were calculated from Eqns (16)–(21), as described in Section 2.2 for exchange between free radicals. For example, in the case of the equivalent spin exchange, when the conditions  $J^2 > D^2$  and  $D^2\tau_c^2 < 1$  are satisfied, the spin-exchange rate constant has the form

$$K_{\text{ex}} = K_D \frac{2J^2\tau_c^2}{1 + 9J^2\tau_c^2}. \quad (36)$$

The limit value of the equivalent spin exchange rate constant is  $K_{\text{ex}} = (2/9)K_D$ .

In the same situation  $J^2 > D^2$  and  $D^2\tau_c^2 < 1$ , the theory predicts the shift of EPR lines to the center of the spectrum by

$$\Delta\omega = \frac{2}{9} \frac{D\tau_c}{1 + 1/(1 + 9J^2\tau_c^2)} K_D C, \quad (37)$$

where  $C$  is the exciton concentration. This line shift was probably observed in [38] in the study of spin exchange between triplet excitons in tetracyanoquinodimethane crystals. In [38], the spin exchange rate was measured from the broadening of spectral lines, line shifts, and the width of the spin-exchange-narrowed spectrum. The exchange rate found from the line shifts proved to be greater than the rate obtained from the broadening of lines. This can be explained by the contribution (37) to the line shift, which was neglected in [38].

**2.3.3 Spin exchange between particles with the spin  $S = 1/2$  and paramagnetic particles with an arbitrary spin.** In [39], the equivalent spin-exchange rate constants were calculated in the approximation of sudden exchange interaction switching for solutions of paramagnetic particles of two types, the spin of particles of the first type being  $S_1 = 1/2$  and the spin  $S_2$  of particles of the second type being arbitrary. Examples of such systems are solutions containing free radicals ( $S_1 = 1/2$ ) and complexes of paramagnetic ions of transition metals ( $S_2 \geq 1/2$ ). It was shown that the rate constants of the equivalent spin exchange for different particles were different. The spin exchange efficiency  $p_{\text{ex}}(S_1)$  for a radical ( $S_1 = 1/2$ ) with ions  $S_2$  and the spin exchange efficiency  $p_{\text{ex}}(S_2)$  for ions with radicals are described by the expressions [39]

$$p_{\text{ex}}(S_1) = \frac{2}{3} S_2(S_2 + 1) \frac{J_0^2\tau_c^2}{1 + (S_1 + S_2)^2 J_0^2\tau_c^2}, \quad (38)$$

$$p_{\text{ex}}(S_2) = \frac{2}{3} S_1(S_1 + 1) \frac{J_0^2\tau_c^2}{1 + (S_1 + S_2)^2 J_0^2\tau_c^2}. \quad (39)$$

For example, for solutions of radicals and bivalent manganese ions (Mn(II)) with the spin  $S_2 = 5/2$ , the ratio of these

efficiencies is

$$\frac{p_{\text{ex}}(S_1)}{p_{\text{ex}}(S_2)} = \frac{S_2(S_2 + 1)}{S_1(S_1 + 1)} = \frac{35}{3},$$

which is quite consistent with the results of EPR experiments [39]. We note that Eqns (38) and (39) can be used only when the spin relaxation times  $T_1$  and  $T_2$  greatly exceed the collision time  $\tau_c$ . This condition is satisfied, for example, for organic radicals, complexes of bivalent manganese, trivalent chromium, bivalent vanadium, trivalent iron, and bivalent copper.

Transition metal ions can also have small paramagnetic relaxation times, shorter than the collision time  $\tau_c$ . For example, the times  $T_1$  and  $T_2$  for Mn(III), Co(II), and Ni(II) complexes are about a few picoseconds, whereas the collision duration is about 0.1 ns. In this case, the influence of the exchange interaction with a paramagnetic complex  $S_2$  on the spin state of a free radical decreases, and fast  $S_2$  spin flips that occur during paramagnetic relaxation tend to eliminate the action of the exchange interaction  $J\mathbf{S}_1\mathbf{S}_2$  on the motion of  $S_1$ . The influence of fast spin–lattice relaxation on the spin exchange efficiency for radicals in solutions containing free radicals ( $S_1 = 1/2$ ) and complexes of paramagnetic ions of transition metals in the approximation of sudden exchange interaction switching was studied in [33, 34]. The radical spin decoherence efficiency was found in the form

$$p_{\text{ex}}(S_1) = \frac{1}{3} S_2(S_2 + 1) J_0^2 (T_1 + T_2) \tau_c \quad (40)$$

instead of (38). A comparison of Eqns (38) and (40) shows that the fast paramagnetic relaxation of the complex decreases the radical spin exchange decoherence efficiency by  $\tau_c/T_1$  times, where  $\tau_c/T_1 \gg 1$ . This conclusion is consistent with experimental data [33, 34].

During collisions between free radicals and paramagnetic complexes with small paramagnetic relaxation times, the spin coherence transfer from the complex to the radical is not expected. In this case (collisions with rapidly relaxing paramagnetic particles), nonequivalent spin exchange occurs.

**2.3.4 Positronium quenching by paramagnetic particles.** An interesting example of spin exchange is the exchange quenching of a positronium by paramagnetic additives [40]. The quenching mechanism is the exchange interaction during the collision of a positronium atom (Ps) with a paramagnetic particle, which induces the transition of a long-lived ortho-positronium (with the lifetime  $\tau_o = 143$  ns) to the short-lived para-state (with the lifetime  $\tau_p = 125$  ps). The exchange interaction causes a mutual electron spin flip in the positronium and in the paramagnetic particle (a radical or a complex). The efficiency of this process was discussed in Section 2.3.3. In [41], the rate constant of the exchange quenching of a positronium by paramagnetic additives was calculated, and the role of the paramagnetic relaxation rate of complexes in the exchange quenching efficiency of Ps was discussed. The obtained results coincide qualitatively with results on the influence of the paramagnetic relaxation rate of particles on the spin exchange efficiency.

The rate constant of positronium quenching by paramagnetic particles with the spin  $S$ , when Ps converters have long paramagnetic relaxation times, i.e.,  $T_1, T_2, \tau_p > \tau_c$ , is

described by the expression [41]

$$K = \frac{1}{6} \frac{W\tau_c}{1 + W\tau_c} K_D. \quad (41)$$

Here,

$$W = \frac{J^2\tau_c S(S+1)}{1 + (\Delta + J/2)^2\tau_c^2} \quad (42)$$

is the rate of the ‘quasi-molecular’ electron spin flip process in the positronium atom caused by the exchange interaction of a paramagnetic particle with the electron of the positronium during a collision. The parameter  $\Delta$  is the singlet–triplet splitting in the positronium atom caused by contact interaction of the electron with positronium. For an arbitrary relation between the time of one collision and the lifetime of para-positronium, the positronium quenching rate constant is [41]

$$K = \frac{W_p\tau_c}{1 + W_p\tau_c(1 + 5\tau/\tau_c)} K_D, \quad (43)$$

$$W_p = \frac{1}{6} \frac{J^2\tau/S(S+1)}{1 + (\Delta + J/2)^2\tau^2}, \quad \frac{1}{\tau} = \frac{1}{\tau_c} + \frac{1}{\tau_p}.$$

The results presented above can be used to analyze the Ps quenching by paramagnetic additives such as organic free radicals and complexes of Cu(II), Fe(III), Mn(II), and Cr(III) ions with relatively long paramagnetic relaxation times. But there are paramagnetic additives with short relaxation times  $T_1, T_2 \sim 10^{-11} - 10^{-13}$  s. Examples are Co(II), Fe(II), and Ni(II) complexes. Similarly to the decrease in the spin exchange efficiency in collisions with particles with short paramagnetic relaxation times (see Eqns (38) and (40)), the exchange interaction induces spin flip in the positronium less efficiently because of the fast spin relaxation of the complex, and therefore such complexes should quench the positronium also less efficiently. Experiments [41] confirm a similar behavior of the Ps conversion rate constant and the spin exchange rate constant found from the shape of EPR spectra of solutions containing free radicals and paramagnetic complexes.

**2.3.5 Influence of the rotational and translational diffusion of particles on the spin exchange in the case of an anisotropic distribution of the spin density in paramagnetic particles.** It is assumed in all calculations of the effective radius and spin exchange rate constant that the exchange integral is independent of the mutual orientation of colliding paramagnetic particles. This assumption is justified if the spin density is uniformly distributed over the ‘surface’ of colliding paramagnetic particles, for example, of ferricyanide ions [42]. However, the spin density in stable nitroxyl radicals, which are often used as spin probes, is concentrated on an oxygen atom, and the spin exchange efficiency is mainly determined by collisions in which just the NO group of the radical approaches the paramagnetic particles most closely. The anisotropic distribution of the spin density on the surface of a paramagnetic particle can be approximately described with a parameter  $f$ , the fraction of the particle surface where the spin density is mainly concentrated. The parameter  $f$  is called the spin-exchange steric factor [23, 42–44].

The rotational and translational diffusion of particles randomly changes the mutual orientation of colliding

particles, thereby changing their exchange interaction in collisions. The influence of the rotational diffusion of particles on the spin exchange efficiency was theoretically studied in the model of sudden exchange interaction switching in [44]. Rotational diffusion is characterized by the correlation time  $\tau_1$  for the orientation of a particle [45, p. 280],

$$\tau_1 = \frac{4\pi\eta a^3}{3k_B T}, \quad (44)$$

where  $\eta$  is the solution viscosity,  $a$  is the van der Waals radius of the particle, and  $k_B$  is the Boltzmann constant.

If rotational diffusion does not have time to change the mutual orientation of colliding particles during the collision time,  $\tau_c < \tau_1$ , the efficiency of the equivalent change between particles with steric factors  $f_1$  and  $f_2$  should be described not by Eqn (11) but by the relation

$$p_{\text{ex}} = \frac{1}{2} \frac{f_1 f_2 J^2 \tau_c^2}{1 + J^2 \tau_c^2}, \quad (45)$$

where  $f_1 f_2 \equiv f_{12}$  is the probability that paramagnetic particles collide with atoms on which the spin density is concentrated. The influence of the rotational diffusion during one collision on the spin exchange efficiency was considered in [44]. For example, in the limit case of a relatively rapid rotation,  $\tau_1 < \tau_c$  and  $d(J)\tau_1\tau_c < 1$ , where  $d(J)$  is the dispersion of  $J$ , the spin exchange efficiency during one collision was obtained in the form

$$p_{\text{ex}} = \frac{1}{2} \frac{\langle J \rangle^2 \tau_c^2 + d(J)\tau_1\tau_c(1 + d(J)\tau_1\tau_c)}{(1 + d(J)\tau_1\tau_c)^2 + \langle J \rangle^2 \tau_c^2}. \quad (46)$$

In this model, the mean value of the exchange integral is  $\langle J \rangle = fJ$ , and the dispersion of the exchange integral in the collision is  $d(J) = f(1-f)J^2$ . In the limit of a strong exchange interaction, when  $f^2 J^2 \tau_c^2 \gg 1$ , we have  $p_{\text{ex}} \rightarrow 1/2$ , and hence  $p_{\text{ex}}$  coincides with the spin exchange efficiency for particles with an isotropic distribution of the spin density.

The role that the repeated contacts and translational diffusion in intervals between repeated collisions play in the spin exchange efficiency was discussed in [42, 43]. It was shown that the average effect that the spin density distribution anisotropy has on the spin exchange due to translational diffusion of particles can be estimated from formulas obtained for the isotropic distribution of the spin density by properly defining the effective collision time  $\tau_c$ . For the isotropic spin density distribution, the total residence time in the exchange interaction region for two particles during one encounter is  $\tau_c = ba/D_{AB}$ , Eqn (14). In the case of an anisotropic spin density distribution, averaging the anisotropic exchange interaction by the translational diffusion of molecules in intervals between repeated collisions at the collision radius  $b$  is described by the expression

$$\tau_c = \frac{f_{12}^{1/2} ba}{D_{AB}} \quad (47)$$

instead of (14). For identical particles with the anisotropic spin density distribution with a steric factor  $f$ , we have  $f_{12} = f^2$  (see (45)), and therefore (47) takes the form  $\tau_c = fba/D_{AB}$ .

The manifestation of the steric factor in the spin exchange between stable radicals attached to rather large molecules was

experimentally studied in [23] and confirmed by a comparison of the spin exchange rates for a nitroxyl radical and its adduct.

#### 2.4 Kinetic equations for the bimolecular spin exchange taking the extended nature of exchange interaction into account

Kinetic equations for the one-particle spin density matrix taking bimolecular collisions and the extended nature of exchange interaction into account were first formulated in [31] and further developed in [21, 25, 46–50].

We consider a diluted solution of paramagnetic particles (spin probes) of two types, A and B. The spin Hamiltonian of such a system can be written in the form

$$\begin{aligned} H &= H_A + H_B + \sum V(|\mathbf{r}_{Ak} - \mathbf{r}_{Bn}|) \\ &= H_A + H_B + \sum V_{AB}(r_{kn}(t)). \end{aligned} \quad (48)$$

In the simplest case,  $H_A$  and  $H_B$  are related to the Zeeman interaction energy of the spin moment of paramagnetic particles with a constant external magnetic field,

$$H_A = \hbar\omega_{0A}S_{Az}, \quad H_B = \hbar\omega_{0B}S_{Bz}, \quad (49)$$

where  $\omega_{0A,B}$  are the Larmor frequencies of spins A and B. We note that in (49), the exchange interaction A–A, B–B does not change the state of the spin ensemble, and therefore we can ignore the bimolecular collisions of identical particles, A + A, B + B.

We assume that the exchange interaction between two spin probes  $A_k$  and  $B_n$  depends only on the distance  $r_{kn}$  between them and has the form

$$V_{AB}(r_{kn}(t)) = \hbar J_0 \exp[-\kappa(r_{kn}(t) - b)] \mathbf{S}_A \mathbf{S}_B. \quad (50)$$

In the spin-exchange theory for solutions,  $r_{kn}$  are treated as external parameters changing randomly in time due to the diffusion of molecules.

The complete description of the spin system of  $N$  paramagnetic particles is given by the multiparticle spin density matrix  $\rho_N(t)$ . Experiments can usually be described with the help of only one-particle or two-particle density matrices, which can be obtained as contractions of  $\rho_N(t)$  over the spin states of  $N - 1$  or  $N - 2$  particles [51]. It is well known from statistical mechanics that partial density matrices for a multiparticle system satisfy a chain of coupled Bogoliubov–Born–Green–Kirkwood–Yvon equations. For a system with spin Hamiltonian (49), the one-particle spin density matrix, for example,  $\rho_A$  for a particle A, satisfies the equation of motion

$$\begin{aligned} \frac{\partial \rho_A(t)}{\partial t} &= -\frac{i}{\hbar} [H_A, \rho_A(t)] \\ &\quad - \frac{1}{V} \text{Tr}_B \sum \int \frac{i}{\hbar} [V_{AB}(r_n(t)), \rho_2(n, t)] d^3 r_n. \end{aligned} \quad (51)$$

Here,  $\rho_2(n, t)$  is the two-particle density matrix of a pair consisting of an arbitrarily chosen molecule A and a molecule B with the  $n$ th number ( $n = 1, 2, \dots, N_B$ ,  $N_B$  being the total number of molecules B). Therefore, the distance  $r_n$  between spins depends only on the number of a B spin. Summation in (51) is performed over all molecules B, integration is performed over the entire volume  $V$ , and  $\text{Tr}_B$  denotes the contraction over the spin variables of particles B. In the thermodynamic limit as  $V, N_B \rightarrow \infty$  under the condition  $N_B/V \rightarrow C_B$ , each molecule B makes on average the same

contribution to the change in the state of the chosen molecule A, and therefore Eqn (51) takes the form

$$\begin{aligned} \frac{\partial \sigma_A(t)}{\partial t} &= -\frac{i}{\hbar} [H_A, \sigma_A(t)] \\ &\quad - C_B \text{Tr}_B \int \frac{i}{\hbar} [V_{AB}(r(t)), \rho_2(t)] d^3 r. \end{aligned} \quad (52)$$

For spins B, the equation for the one-particle spin matrix  $\sigma_B$  is obtained from Eqn (52) by the replacement  $A \rightarrow B$  and vice versa. As noted in Section 2.2 in connection with the model of sudden collisions (see Eqn (16)), the one-particle density matrix changes on the time scale of the diffusion of particles between collisions with different molecules, whereas the last term in (52) changes on a considerably smaller collision time scale.

We introduce one-particle density matrices  $\sigma_A$  and  $\sigma_B$  averaged over the collision time interval. By averaging (52) on the collision time scale, we obtain

$$\begin{aligned} \frac{\partial \sigma_A(t)}{\partial t} &= -\frac{i}{\hbar} [H_A, \sigma_A(t)] \\ &\quad - C_B \text{Tr}_B \left\langle \int \frac{i}{\hbar} [V_{AB}(r(t)), \sigma_2(t)] d^3 r \right\rangle, \end{aligned} \quad (52a)$$

where the angular brackets denote averaging over all possible realizations of the random process  $r(t)$ .

The equation for the pair density matrix  $\rho_2(n, t)$  can be obtained similarly; it contains the three-particle density matrix [51]:

$$\begin{aligned} \frac{\partial \rho_2(1, t)}{\partial t} &= -\frac{i}{\hbar} [H_A + H_B + V_{AB}(r_1(t)), \rho_2(1, t)] \\ &\quad + F(\rho_3(1, 2, t)). \end{aligned} \quad (53)$$

The last term in the right-hand side of (53) contains the three-particle density matrix  $\rho_3(1, 2, t)$  of three particles, A,  $B_1$ , and  $B_2$ , and  $r_1$  and  $r_2$  are the respective distances between particles in pairs A– $B_1$  and A– $B_2$ . We assume that the spin concentration is sufficiently low,  $(4/3)\pi r_{\text{ex}}^3 C_B \ll 1$ , and triple spin collisions can be ignored. Therefore, we truncate the chain of equations and use the equation

$$\frac{\partial \rho_2(t)}{\partial t} = -\frac{i}{\hbar} [H_A + H_B + V_{AB}(r(t)), \rho_2(t)] \quad (54)$$

for the pair density matrix. Equation (54) depends on the random process  $r(t)$ . This stochastic equation should be solved for each possible realization of the random process  $r(t)$ , and then the results should be averaged. However, because we assume that  $r(t)$  is an external parameter independent of the spin state, the problem can be reformulated such that instead of stochastic equation (54), equations with time-independent coefficients must be solved [31, 47, 52]. This reformulation of the problem is in fact based on the ergodic hypothesis about the equivalence of averaging over a long time interval and over an ensemble. Therefore, we divide the ensemble of pairs of particles A and B into subensembles of pairs with a specified distance  $r$  between partners A and B in a pair. We introduce the partial two-particle spin density matrix  $\sigma_2(t|r)$  for each subensemble of pairs. This *pair* spin density matrix changes for two reasons. On the one hand, the state of a pair of spins changes due to the spin dynamics under the action of the spin Hamiltonian  $H_{AB}(r) \equiv H_A + H_B + V_{AB}(r)$  of the given pair subensemble with the specified

distance  $r$  between partners in the pair A–B. The change in the pair spin density matrix caused by the spin dynamics is described by the expression

$$\left(\frac{\partial\sigma_2(t|r)}{\partial t}\right)_{\text{spin dynamics}} = -\frac{i}{\hbar} [H_A + H_B + V_{AB}(r), \sigma_2(t|r)]. \quad (55)$$

Here, the distance  $r$  between particles in a pair is no longer a stochastic process but an external parameter.

On the other hand, due to the diffusion of molecules, each pair can transfer from one subensemble of pairs to another. Changes in  $\sigma_2(t|r)$  caused by molecular diffusion can be found from the continuity equation

$$\left(\frac{\partial\sigma_2(t|r)}{\partial t}\right)_{\text{diffusion}} + \text{div}_r(\mathbf{j}(\sigma_2(t|r))) = 0. \quad (56)$$

Here,  $\mathbf{j}(\sigma_2(t|r))$  is the flux of pairs in the configuration space. For the continuous diffusion model for neutral molecules,

$$\mathbf{j}(\sigma_2(t|r)) = -D_{AB}\nabla_r\sigma_2(t|r). \quad (57)$$

In solutions of charged particles A and B in electrolytes, the flow is induced not only by the diffusion of particles but also by their drift caused by electrostatic interaction [7, 19].

The total change in the pair partial spin density matrix is described by the sum of these two contributions:

$$\frac{\partial\sigma_2(t|r)}{\partial t} = -\frac{i}{\hbar} [H_{AB}(r), \sigma_2(t|r)] - \text{div}_r(\mathbf{j}(\sigma_2(t|r))). \quad (58)$$

In the model of continuous diffusion of molecules, this kinetic equation takes the form

$$\frac{\partial\sigma_2(t|r)}{\partial t} = -\frac{i}{\hbar} [H_A + H_B + V_{AB}(r), \sigma_2(t|r)] + D_{AB}\Delta(\sigma_2(t|r)). \quad (59)$$

We note that for a Markov random process, Eqns (58) and (59) can be obtained by the direct summation of solutions of stochastic equation (54) for all possible realizations of the random process (see, e.g., [31, 47, 52]).

To obtain the kinetic equation for a one-particle spin density matrix, the pair density matrix in Eqn (54) should be expressed in terms of one-particle density matrices. Kinetic equations describe the behavior of the system at times exceeding the collision time of particles,  $t > \tau_c$ . For these times, we seek the solution of Eqn (59) for  $\sigma_2(t|r)$  in the form [51]

$$\sigma_2(t|r) \approx G(r)\sigma_A(t)\sigma_B(t). \quad (60)$$

After substituting (60) in Eqn (59), the left-hand side of (59) takes the form

$$Y = G(r)\frac{\partial\sigma_A(t)}{\partial t}\sigma_B(t) + G(r)\sigma_A(t)\frac{\partial\sigma_B(t)}{\partial t}. \quad (61)$$

If we now substitute expressions for  $\partial\sigma_{A,B}/\partial t$  here (see (52a)), quadratic terms containing  $\sigma_A(t)\sigma_B(t)$  and cubic terms containing  $\sigma_A(t)\sigma_B(t)\sigma_B(t)$  and  $\sigma_A(t)\sigma_A(t)\sigma_B(t)$  appear. Cubic terms correspond to trimolecular collisions, which we disregard. Therefore, in (58) we set

$$\begin{aligned} \frac{\partial\sigma_A(t)}{\partial t} &\approx -\frac{i}{\hbar} [H_A, \sigma_A(t)] \equiv -iQ_{0A}\sigma_A(t), \\ \frac{\partial\sigma_B(t)}{\partial t} &= -\frac{i}{\hbar} [H_B, \sigma_B(t)] \equiv -iQ_{0B}\sigma_B(t). \end{aligned} \quad (62)$$

As a result, we obtain the equations for the operator  $G(r)$  [31]

$$W(r)G(r) + [Q_0, G(r)] + D_{AB}\Delta G(r) = 0, \quad (63)$$

$$W(r)_{ik,lm} = -iJ(r)[(S_A S_B)_{mk}\delta_{li} - (S_A S_B)_{il}\delta_{km}],$$

$$Q_0 = Q_{0A} + Q_{0B}, \quad (64)$$

$$Q_{0ik,lm} = -i[(H_A + H_B)_{mk}\delta_{li} - (H_A + H_B)_{il}\delta_{km}].$$

We note that Eqn (63) is obtained for the model of continuous diffusion of particles. For the sudden exchange interaction model, Eqn (63) reduces to (20).

We formulate boundary conditions for  $G(r)$ . When the partners in a pair are separated, the correlation between their states must weaken [51]. Therefore, we impose the condition

$$G(r) \rightarrow E \text{ as } r \rightarrow \infty. \quad (65)$$

At the closest approach radius, particles are completely reflected. This gives the second boundary condition: the flow  $\sigma_2(t|r)$  through a sphere with the radius  $r = b$  must be zero. For neutral particles, we have

$$\nabla_r G(r = r_0) = 0. \quad (66)$$

We introduce the collision superoperator

$$P = \int W(r)G(r) d^3\mathbf{r}. \quad (67)$$

We note that in some particular cases, when the term  $-i[Q_0, G(r)]$  can be ignored or is zero, collision superoperator (67) can be written in a different form [31, 46]:

$$P = -D_{AB} \int \Delta G(r) d^3\mathbf{r}. \quad (68)$$

Thus, we obtain kinetic equations

$$\frac{\partial\sigma_A(t)}{\partial t} = -\frac{i}{\hbar} [H_{0A}, \sigma_A(t)] + C_B \text{Tr}_B(P\sigma_A(t)\sigma_B(t)), \quad (69)$$

$$\frac{\partial\sigma_B(t)}{\partial t} = -\frac{i}{\hbar} [H_{0B}, \sigma_B(t)] + C_A \text{Tr}_A(P\sigma_A(t)\sigma_B(t)) \quad (70)$$

for one-particle density matrices.

We note that in the model discussed in Section 2.2, when a pair of particles enters some ‘cell’ at the collision distance  $r_0$  where a constant exchange interaction switches on abruptly or when the pair leaves the ‘cell’ and the interaction switches off, a jump-like passage through the interaction region is assumed. In this case, spin pairs can be divided into two subensembles. In the first one, spins are located in the ‘cell’ at the collision distance, and in the second, the distance between spins exceeds the collision distance, and hence the pair is located outside the ‘cell’. In this model, the kinematic flux of the pair density matrix is not specified by an equation like (57), and for the density matrix of pairs in the ‘cell’, instead of (59) and (63), we have the equation [31]

$$\frac{\partial\sigma_2(t|r_0)}{\partial t} = -\frac{i}{\hbar} [H_A + H_B + V_{AB}(r_0), \sigma_2(t|r_0)]$$

$$- \frac{1}{\tau_c} (\sigma_2(t|r_0) - \sigma_A(t)\sigma_B(t)),$$

$$W(r_0)G(r_0) + [Q_0, G(r_0)] - \frac{1}{\tau_c} (G(r_0) - E) = 0,$$

where  $E$  is the unit operator. This equation coincides with (20).

Equations (69) and (70) are kinetic equations for the spin density matrix of paramagnetic particles in diluted solutions, taking the bimolecular spin exchange into account. Equations (63) and (68) are used to calculate effective spin exchange radii taking the extended nature of the exchange interaction into account. The kinetic equations obtained are fundamentally simplified if systems are considered in a state close to equilibrium (see (21)). Substituting (21) in (69), (70) and keeping only the density matrix terms linear in small deviations, we obtain

$$\begin{aligned} \frac{\partial \Delta \sigma_A(t)}{\partial t} &= -\frac{i}{\hbar} [H_{0A}, \Delta \sigma_A(t)] \\ &+ C_B \text{Tr}_B (P \Delta \sigma_A(t) \sigma_{\text{Beq}} + P \sigma_{\text{Aeq}} \Delta \sigma_B(t)), \\ \frac{\partial \Delta \sigma_B(t)}{\partial t} &= -\frac{i}{\hbar} [H_{0B}, \Delta \sigma_B(t)] \\ &+ C_A \text{Tr}_A (P \Delta \sigma_A(t) \sigma_{\text{Beq}} + P \sigma_{\text{Aeq}} \Delta \sigma_B(t)). \end{aligned} \quad (71)$$

In EPR experiments, the averaged characteristics of the total molecular ensemble are measured. A constant external magnetic field  $\mathbf{B}_0$  is usually assumed to be directed along the  $z$  axis of the coordinate system. In most EPR experiments, the observed magnetization component of the system is perpendicular to the constant magnetic field direction, i.e., the  $M_x$  and  $M_y$  magnetization components.

The derivation of equations for the magnetization of the system is illustrated below for a solution of paramagnetic particles A and B with one unpaired electron. We consider a model situation where the spin Hamiltonians of particles A and B are specified by Eqns (22). Then the eigenfunctions of operators  $H_A$  and  $H_B$  are  $S_{Az}$  and  $S_{Bz}$ . The spin density matrix in the basis of eigenfunctions of the spin operator  $S_z$  has the form

$$\rho = \{(\rho_{1/2, 1/2}, \rho_{1/2, -1/2}), (\rho_{-1/2, 1/2}, \rho_{-1/2, -1/2})\}.$$

The diagonal elements of the density matrix characterize the populations of spin states, and the nondiagonal elements describe the quantum spin coherence. For particles with the spin  $S = 1/2$  considered here, we have

$$\begin{aligned} \langle S_x - iS_y \rangle &= \text{Tr}((S_x - iS_y)\rho) = \rho_{1/2, -1/2}, \\ \langle S_z \rangle &= \text{Tr}(S_z \rho) = \frac{1}{2}(\rho_{1/2, 1/2} - \rho_{-1/2, -1/2}). \end{aligned} \quad (72)$$

The macroscopic magnetization of particles A and B is expressed in terms of one-particle spin matrices. For example,

$$M_{A-} = C_A \text{Tr}_A [(S_{Ax} - iS_{Ay})\rho_A(t)], \quad (73)$$

$$M_{B-} = C_B \text{Tr}_B [(S_{Bx} - iS_{By})\rho_B(t)].$$

Multiplying the first of Eqns (71) by  $C_A$  and the second by  $C_B$ , we obtain kinetic equations for spin magnetization, which take the simplest form when  $|\omega_{0A} - \omega_{0B}| \tau_c < 1$  and the equivalent spin exchange occurs during the bimolecular encounter of particles A and B. In this case, we obtain the equations (cf. (9))

$$\begin{aligned} \frac{\partial M_{A-}}{\partial t} &= -i\omega_{0A} M_{A-} - K_{\text{ex}} C_B M_{A-} + K_{\text{ex}} C_A M_{B-}, \\ \frac{\partial M_{B-}}{\partial t} &= -i\omega_{0B} M_{B-} + K_{\text{ex}} C_B M_{A-} - K_{\text{ex}} C_A M_{B-}, \end{aligned}$$

$$\begin{aligned} \frac{\partial M_{Az}}{\partial t} &= -K_{\text{ex}} C_B M_{Az} + K_{\text{ex}} C_A M_{Bz}, \\ \frac{\partial M_{Bz}}{\partial t} &= K_{\text{ex}} C_B M_{Az} - K_{\text{ex}} C_A M_{Bz}. \end{aligned} \quad (74)$$

## 2.5 Calculations of the effective spin exchange radius for arbitrary-spin particles with the extended nature of the exchange interaction and the diffusive propagation of particles through the interaction region taken into account

The effective radii of the bimolecular equivalent spin exchange for particles with arbitrary spins were calculated in [25] with the help of kinetic equations presented in Section 2.4. The spin Hamiltonian of the exchange interaction is described by Eqns (1) and (15). It is assumed in [25] that in nonviscous liquids and in the case of fast rotational diffusion, the so-called zero field splitting of energy levels of paramagnetic particles averages to zero. Therefore, it is assumed that the exchange interaction in the region of collisions of particles is strong enough to allow all the other spin interactions to be disregarded. Based on these assumptions, analytic expressions have been obtained for the effective radii of the equivalent spin exchange between particles with arbitrary spins [25]. For example, the transverse components of the magnetization of the subensembles of spins A and B are described by the kinetic equations

$$\begin{aligned} \frac{\partial M_{A-}}{\partial t} &= -i\omega_{0A} M_{A-} - K_A C_B M_{A-} + K_B C_A M_{B-}, \\ \frac{\partial M_{B-}}{\partial t} &= -i\omega_{0B} M_{B-} + K_A C_B M_{A-} - K_B C_A M_{B-}. \end{aligned} \quad (75)$$

These equations look similar to Eqns (74). But unlike the spin exchange between free radicals with the spin  $S = 1/2$  (74), in the case of arbitrary spins of colliding particles, the equivalent spin exchange is specified in (75) not by a single constant  $K_{\text{ex}}$ , as in (74), but by two spin exchange rate constants  $K_A$  and  $K_B$ :

$$\begin{aligned} K_A &= 4\pi D_{AB} \sum_{S=\text{mod}(S_A-S_B)+1}^{S_A+S_B} \frac{N(S)}{S_A(S_A+1)} r_{\text{ex}}(S) \equiv 4\pi R_{\text{exA}} D_{AB}, \\ K_B &= 4\pi D_{AB} \sum_{S=\text{mod}(S_A-S_B)+1}^{S_A+S_B} \frac{N(S)}{S_B(S_B+1)} r_{\text{ex}}(S) \equiv 4\pi R_{\text{exB}} D_{AB}, \end{aligned} \quad (76)$$

where

$$\begin{aligned} r_{\text{ex}}(S) &= \frac{1}{2} \left\{ b + \frac{1}{\kappa} \left[ \ln \left( \frac{|J_0|S}{D_{AB}\kappa^2} \right) + 2C - C'_1 \right] \right\}, \\ C'_1 &= \frac{\pi \text{Re}[N_1(2x_0)x_0\kappa b - 2N_0(2x_0)]}{I_1(2x_0)x_0\kappa b - 2I_0(2x_0)}, \\ x_0 &= \left( \frac{|J_0|S}{D_{AB}\kappa^2} \right)^{1/2} \exp \frac{i\pi}{4}, \end{aligned}$$

and  $C \approx 0.57721566$  is the Euler constant. Summation over  $S$  in these equations is performed with the increment 1. We can see from Eqns (76) that the ratio of spin exchange kinetic constants  $K_A$  and  $K_B$  is determined by the ratio of the squares of spins of the partners,

$$\frac{K_A}{K_B} = \frac{S_B(S_B+1)}{S_A(S_A+1)}. \quad (77)$$

This coincides with the result obtained for the model of sudden exchange interaction switching for collisions of paramagnetic particles with the spin  $S = 1/2$  and particles with arbitrary spins, Eqns (38) and (39).

For  $[|J_0|S/(D_{AB}\kappa^2)]^{1/2} \gg 1$ ,  $C'_1 \rightarrow 0$  in (76), and the effective radius depends on the exchange integral logarithmically:

$$r_{\text{ex}}(S) \approx \frac{1}{2} \left\{ b + \frac{1}{\kappa} \left[ \ln \left( \frac{|J_0|S}{D_{AB}\kappa^2} \right) + 2C \right] \right\}. \quad (78)$$

In this case, the characteristic collision time of particles is determined by the time of diffusive propagation through a region with the radius  $\sim 1/\kappa$ . Because the exchange integral in the model under study decreases exponentially, for large values of  $J_0$  and a quite small steepness of its decrease with increasing distance, a logarithmic dependence of the effective spin exchange radius on the interaction strength and the diffusion coefficient should be expected. These expectations are indeed justified (see (78)). If the exchange integral decreases rapidly, i.e.,  $b > 1/\kappa$ , the spin exchange occurs in a thin layer  $\sim 1/\kappa$  in thickness, and the characteristic collision time is  $\tau_c \approx b/(D_{AB}\kappa)$  (see (76)). These theoretical results are illustrated in Fig. 1 by the dependences of the effective spin exchange radius on the parameters of the exchange integral and the mutual diffusion coefficient of molecules.

As the mutual diffusion coefficient of paramagnetic particles increases, the effective spin exchange radius always decreases, as expected. Indeed, the greater the mobility of molecules in solutions, the shorter is the residence time of a pair of colliding particles in the exchange interaction region. As a result, the effect of exchange interaction decreases. The effective spin exchange radius always increases with increasing the exchange integral  $J_0$  at the collision radius and with decreasing the steepness of the exchange integral decay with the distance between colliding particles. These results are expected qualitatively and are quantitatively predicted theoretically.

Spin probes commonly used in experiments are free nitroxyl radicals. Therefore, we here present explicit expressions for the effective spin exchange radius for this case [25, 46]. We have

$$r_{\text{ex}} = \frac{b}{2} + \text{Re} \left[ \frac{C + \ln(x_0/2)}{\kappa} - \frac{c}{2} \right], \quad (79)$$

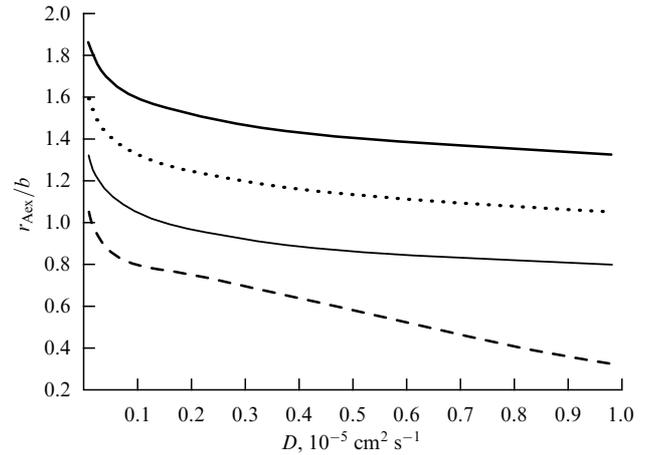
where

$$x_0 = 2 \left( -\frac{iJ_0}{D\kappa^2} \right)^{1/2}, \quad c = \frac{\pi}{\kappa} \frac{N_1(x_0)x_0\kappa b - 2N_0(x_0)}{I_1(x_0)x_0\kappa b - 2I_0(x_0)},$$

$C$  is the Euler constant,  $D$  is the mutual diffusion coefficient for two colliding particles,  $J_0$  is the exchange integral at the collision radius, and  $I_k$  and  $N_k$  are Bessel functions of the first and second kinds.

As could be expected, in the limit of relatively small values of the exchange integral  $J_0$  and a very abrupt decrease in the exchange integral with increasing the distance between particles, when the condition  $|x_0|^2 = 4J_0/(D\kappa^2) \ll 1$  is satisfied, the effective spin exchange radius can be written in the same form as in the approximation of sudden exchange interaction switching (see (11), (27)):

$$r_{\text{ex}} \approx \frac{b}{2} \frac{J_0^2 \tau^2}{1 + J_0^2 \tau^2}, \quad \tau = \frac{b}{D\kappa}. \quad (80)$$



**Figure 1.** Dependences of  $r_{\text{Aex}}/b$  (see Eqns (76)) on the mutual diffusion coefficient  $D_{AB}$  for different values of the exchange integral:  $J_0 = 10^{10}$  (dashed curve),  $J_0 = 10^{11}$  (thin solid curve),  $J_0 = 10^{12}$  (dotted curve), and  $J_0 = 10^{13}$  [rad s $^{-1}$ ] (thick solid curve). Calculations are performed for  $S_A = 1/2$ ,  $S_B = 1$ ,  $b = 0.5$  nm,  $D_{AB}$  ranges within  $10^{-7}$ – $10^{-5}$  cm $^2$  s $^{-1}$ , and  $\kappa = 10^8$  cm $^{-1}$ .

Equation (80) coincides in its form with Eqn (11) in the approximation of sudden exchange interaction switching. But the total time  $\tau$  in (80) includes the first and all the repeated collisions of a pair of particles in the region between two spheres with the radii  $b$  and  $b + 1/\kappa$ .

In the limit of a strong exchange interaction, when  $4J_0/(D\kappa^2) > 1$ , the spin exchange is efficient not only when particles come closest together, but also at distances  $r > b$ . Because of the extended nature of the exchange integral, the effective radius of the equivalent spin exchange can exceed the maximum possible value  $b/2$  predicted for these systems by the theory based on the model of sudden exchange interaction switching, Eqns (11) and (27). We also note that the spin exchange rate constant is not a linear function of the mutual diffusion coefficient of paramagnetic particles, unlike the rate constant of bimolecular collisions found by Smoluchowski, Eqn (6).

## 2.6 Spin exchange between charged particles with the spin $S = 1/2$ in electrolytes

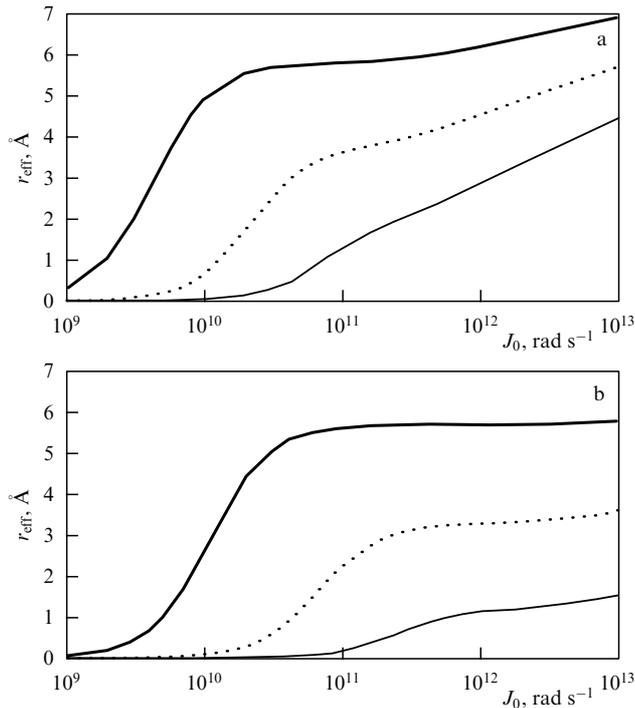
A consistent theory of spin exchange between charged paramagnetic particles in electrolytes was developed in [19]. The Coulomb interaction was considered taking the Debye screening of charges in electrolytes into account:

$$U(r) = \frac{q_A q_B}{\epsilon r} \exp \left( -\frac{r}{r_D} \right). \quad (81)$$

Here,  $q_A$  and  $q_B$  are the charges of particles,  $\epsilon$  is the medium permittivity, and  $r_D$  is the Debye screening radius. The flux of pairs in the  $\mathbf{r}$  space (see (56) and (57)) is then described by the expression

$$\mathbf{j}(\mathbf{r}) = -D_{AB} \text{grad}_r(\rho(t|\mathbf{r})) + \rho(t|\mathbf{r})\mathbf{v}(\mathbf{r}), \quad (82)$$

where  $\mathbf{v}(\mathbf{r}) = \mu\mathbf{F}(\mathbf{r}) = -[D_{AB}/(k_B T)] \text{grad } U(\mathbf{r})$ . Kinetic equations for spin density matrices were formulated for this situation based on considerations presented in Section 2.4. Because of the change in the flux of pairs in passing from neutral molecules to charged particles, Eqn (63) for the superoperator  $G(\mathbf{r})$  changes. Instead of (63), we obtain the



**Figure 2.** Influence of charges on the effective spin exchange radius. Calculations are performed for  $r_D = 1$  nm,  $b = 0.6$  nm,  $\varepsilon = 20$ ,  $D_{AB} = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. The exchange integral decay slope is (a)  $\kappa = 10^8$  cm<sup>-1</sup> and (b)  $\kappa = 3 \times 10^8$  cm<sup>-1</sup>. The abscissa scale is logarithmic, the exchange integral value  $J_0$  is chosen in the interval from  $10^9$  to  $10^{13}$  rad s<sup>-1</sup>.

equation

$$W(r)G(r) + [Q_0, G(r)] + L(r)G(r) = 0, \quad (83)$$

where

$$L(r) = D_{AB} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - D_{AB} \frac{q_A q_B}{\varepsilon k_B T r^2} \left[ \left( 1 + \frac{r}{r_D} \right) \frac{\partial}{\partial r} - \frac{r}{r_D^2} \right] \exp \left( -\frac{r}{r_D} \right).$$

Accordingly, for charged particles, the boundary condition of the zero flux of pairs at the collision radius

$$\frac{\partial G(b)}{\partial r} - \frac{q_A q_B}{\varepsilon k_B T b^2} \left( 1 + \frac{b}{r_D} \right) \exp \left( -\frac{b}{r_D} \right) = 0 \quad (84)$$

is to be used for the operator  $G(r)$ . The obtained kinetic equations were solved numerically and the effective radii of spin exchange between charged particles of the same sign and with opposite signs were calculated. As expected, the effective spin exchange radius for oppositely charged particles is greater than for neutral particles, while the effective spin exchange radius for particles of the same sign is smaller than for neutral particles.

The effective spin exchange radii for oppositely charged particles, neutral particles, and particles with the same charge are compared in Fig. 2. The thick curves in Fig. 2 correspond to oppositely charged particles, thin curves to particles of the same charge, and dotted curves to neutral particles. We can see from Fig. 2 that the influence of the charge of particles on spin exchange is especially strong in the region of weak exchange interaction  $J_0 < 10^{11}$  rad s<sup>-1</sup>. We note that for a large slope of the exchange integral decay (Fig. 2b), the effective spin decay radius flattens out upon increasing the exchange integral  $J_0$  at the collision radius (in the chosen

interval of exchange integral values). For more gentle slopes of the exchange integral decay (Fig. 2a), the effective spin exchange radius does not flatten out when increasing the exchange integral  $J_0$  but increases logarithmically. The results of numerical calculations are consistent with experimental data [21, 22].

### 3. Paramagnetic relaxation caused by the spin–spin dipole–dipole interaction of paramagnetic particles in liquids

The shape of EPR spectra changes with changing the spin concentration not only due to the exchange interaction. The dipole–dipole interaction must also be taken into account. Unlike the exchange interaction, the dipole–dipole interaction has a long-range nature.

As a rule, the exact values of the exchange integral for colliding particles in solutions and its dependence on the distance and mutual orientation of particles are unknown, and they should be calculated or estimated, for example, from EPR spectra [12, 13]. For the dipole–dipole interaction, the situation is much better, because the spin Hamiltonian is known. At distances exceeding van der Waals radii, calculations can be performed in the point dipole approximation. The common feature of these interactions is the dependence of their contribution to the motion of spins on the concentration of paramagnetic particles. In experiments, the problem appears of separating the contribution of bimolecular collisions during which the spin exchange occurs. We note that along with inducing the mutual spin flip in two colliding particles, the dipole–dipole interaction can also cause a spin flip only in one of the colliding particles or the simultaneous spin flip of two identical polarized spins.

The theory of paramagnetic relaxation caused by the dipole–dipole interaction of spins in diluted solutions was considered many times in the literature. It would seem that there is no need to reproduce it here. However, the derivation of kinetic equations for the spin density matrix in the first papers in this field was based on an unjustified approximation (see, e.g., Eqns (VIII.35) and (VIII.36) in [45]). As a result, no terms describing the spin coherence transfer between spins with different resonance frequencies have remained in the kinetic equation. Correct equations obtained in [53] remained unnoticed for a long time, but then were confirmed in experiments [18] and were recently further developed [11, 24, 50, 51]. The state-of-the-art theory is briefly presented in Section 3.2.

#### 3.1 Spin Hamiltonian of the dipole–dipole interaction of paramagnetic particles

We consider a system with the spin Hamiltonian

$$H = \hbar \sum \omega_k S_{kz} + \hbar \sum H_{d-d}(k, n), \quad (85)$$

where  $\omega_k$  are the Zeeman frequencies of paramagnetic particles. We note that the difference between frequencies can be related not only to the different  $g$ -factors of paramagnetic particles but also to the difference between local magnetic fields caused by the hyperfine interaction with magnetic nuclei or between other spin-dependent interactions of individual particles. The second term in the right-hand side of (85) describes the dipole–dipole spin–spin interaction between all possible pairs of particles. In the problem of paramagnetic relaxation in liquids considered here, the contributions from interactions of all pairs to

relaxation are additive. Therefore, we can consider the relaxation for one pair of spins and then sum the contributions from all pairs.

We consider the spin Hamiltonian for two arbitrarily chosen spins in the form (see [45])

$$H = \hbar(H_0 + H_{d-d}), \quad H_0 = \omega_1 S_{1z} + \omega_2 S_{2z}, \quad (86)$$

$$H_{d-d} = \sum F^q(t) A^q,$$

where

$$A^0 = \alpha \left[ -\frac{2}{3} S_{1z} S_{2z} + \frac{1}{6} (S_{1+} S_{2-} + S_{1-} S_{2+}) \right],$$

$$A^1 = \alpha (S_{1z} S_{2+} + S_{1+} S_{2z}), \quad A^{-1} = \alpha (S_{1z} S_{2-} + S_{1-} S_{2z}),$$

$$A^2 = \frac{\alpha (S_{1+} S_{2+})}{2}, \quad A^{-2} = \frac{\alpha (S_{1-} S_{2-})}{2}, \quad \alpha = -\frac{3}{2} \gamma_1 \gamma_2 \hbar, \quad (87)$$

$$F^{(0)}(t) = \frac{1 - 3 \cos^2 \theta}{r^3}, \quad F^{(+1)}(t) = \sin \theta \cos \theta \frac{\exp(-i\varphi)}{r^3},$$

$$F^{(-1)}(t) = \sin \theta \cos \theta \frac{\exp(i\varphi)}{r^3},$$

$$F^{(2)}(t) = \sin^2 \theta \frac{\exp(-i2\varphi)}{r^3}, \quad F^{(-2)}(t) = \sin^2 \theta \frac{\exp(i2\varphi)}{r^3}.$$

Here,  $r$  is the distance between spins in a pair and  $\theta$  is the angle between the radius vector  $\mathbf{r}$  connecting spins in the pair and the external magnetic field direction (the  $z$  axis). Due to translational diffusion, the relative spatial position of spins changes. As a result,  $F^q(t)$  randomly changes with time.

### 3.2 Kinetic equations describing the electron paramagnetic relaxation in liquids caused by the dipole–dipole interaction

The equation of motion for the density matrix of a separated spin pair is a differential equation with coefficients that are random processes:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H(t), \rho]. \quad (88)$$

Solving Eqn (88) up to quadratic terms in the dipole–dipole interaction  $H_{d-d}$  and averaging over all possible trajectories of the relative motion of two spins, we obtain the equation for the elements of the two-spin density matrix [45, 53]:

$$\frac{\partial \rho_{\alpha\alpha'}}{\partial t} = -\frac{i}{\hbar} [H_0, \rho]_{\alpha\alpha'} + \sum R_{\alpha\alpha', \beta\beta'} \rho_{\beta\beta'}. \quad (89)$$

An unjustified approximation that is widely used restricts summation over  $\beta\beta'$  in the right-hand side of (89) by states with energies  $\hbar\beta$  and  $\hbar\beta'$  satisfying the condition  $\beta - \beta' = \alpha - \alpha'$ .

In Eqn (89),  $\alpha$  and  $\beta$  are eigenstates of the spin Hamiltonian  $H_0$  of a spin pair, and kinetic coefficients  $R_{\alpha\alpha', \beta\beta'}$  are expressed in terms of  $H_{d-d}(t)$  as

$$R_{\alpha\alpha', \beta\beta'} = \frac{1}{2} [J_{\alpha\beta, \alpha'\beta'} (\alpha' - \beta') + J_{\alpha\beta, \alpha'\beta'} (\alpha - \beta) - \delta_{\alpha'\beta'} \sum J_{\gamma\beta\gamma\alpha} (\gamma - \beta) - \delta_{\alpha\beta} \sum J_{\gamma\alpha'\gamma\beta'} (\gamma - \beta')], \quad (90)$$

$$J_{\alpha\alpha', \beta\beta'}(\omega) = \int_{-\infty}^{\infty} G_{\alpha\alpha', \beta\beta'}(\tau) \exp(-i\omega\tau) d\tau,$$

$$G_{\alpha\alpha', \beta\beta'}(\tau) = \left\langle \left\langle \alpha | H_{d-d}(t) | \alpha' \right\rangle \left\langle \beta' | H_{d-d}(t + \tau) | \beta \right\rangle \right\rangle_t.$$

The angular brackets in the right-hand side of the last equation denote averaging over all the possible trajectories of the random walk of a pair of particles. Thus, kinetic parameters  $R_{\alpha\alpha', \beta\beta'}$  in (90) are expressed in terms of the spectral densities  $J_{\alpha\alpha', \beta\beta'}(\omega)$  of correlation functions of the randomly changing dipole–dipole interaction Hamiltonian.

The density matrix of a spin pair in relaxation kinetic equation (89) can be approximated by the direct product of one-spin density matrices:  $\rho(1, 2) \approx \rho(1)\rho(2)$ . Relaxation under conditions close to equilibrium can be considered by representing one-spin density matrices in the form of the equilibrium density matrix  $\rho_0$  and an addition  $\sigma$  describing small deviations of the spin ensemble state from equilibrium (see (21)). Using Eqns (89) and (90) and linearizing the obtained equation with respect to  $\sigma$ , we arrive at linear kinetic equations for one-spin density matrices, which yield kinetic equations for the partial magnetizations of subensembles of isochromatic spins. For example, for solutions of free radicals with EPR spectra consisting of a number of hyperfine components, we obtain the system of kinetic equations presented below [11, 21, 22, 24]. We note that in Eqn (21) in [24], the contribution from the dipole–dipole interaction between spins with the same frequency is erroneously absent. The correct equations are presented in [11, 21, 22]:

$$\begin{aligned} \frac{\partial M_{k-}}{\partial t} &= -i\omega_k M_{k-} - \frac{M_{k-}}{T_2} \\ &\quad - M_{k-} \sum \frac{\varphi_n}{T_2(k, n)} - \varphi_k \sum \frac{M_{n-}}{T_2'(k, n)}, \\ \frac{\partial M_{kz}}{\partial t} &= -\frac{M_{kz} - M_{k0}}{T_1} \\ &\quad - M_{kz} \sum \frac{\varphi_n}{T_1(k, n)} - \varphi_k \sum \frac{M_{nz}}{T_1'(k, n)}. \end{aligned} \quad (91)$$

Here,  $M_{k-} \equiv M_{kx} - iM_{ky}$ ,  $M_{kz}$  are the transverse and longitudinal components of the magnetization vector of isochromatic spins with the frequency  $\omega_k$ ,  $T_2$  and  $T_1$  are the respective spin decoherence and spin–lattice relaxation times,  $\varphi_k$  is the statistical weight of isochromatic spins, and  $M_{k0}$  is the equilibrium magnetization of spins with the frequency  $\omega_k$ . Parameters characterizing the contribution of the dipole–dipole interaction to the paramagnetic relaxation are described by the expressions

$$\begin{aligned} \frac{1}{T_2(k, n)} &= \frac{1}{8} \gamma^4 \hbar^2 C \left[ J^{(0)}(0) + \frac{1}{4} J^{(0)}(\omega_k - \omega_n) \right. \\ &\quad \left. + \frac{9}{2} J^{(1)}(\omega_n) + 9J^{(1)}(\omega_k) + \frac{9}{4} J^{(2)}(\omega_k + \omega_n) \right], \\ \frac{1}{T_2'(k, n)} &= \frac{1}{16} \gamma^4 \hbar^2 C [J^{(0)}(0) + J^{(0)}(\omega_k - \omega_n) \\ &\quad + 9J^{(1)}(\omega_k) + 9J^{(1)}(\omega_n)], \\ \frac{1}{T_1(k, n)} &= \frac{1}{16} \gamma^4 \hbar^2 C [J^{(0)}(\omega_k - \omega_n) + 18J^{(1)}(\omega_k) \\ &\quad + 9J^{(2)}(\omega_k + \omega_n)], \\ \frac{1}{T_1'(k, n)} &= \frac{1}{16} \gamma^4 \hbar^2 C [-J^{(0)}(\omega_k - \omega_n) + 9J^{(2)}(\omega_k + \omega_n)]. \end{aligned} \quad (92)$$

If diffusion is described by the continuous diffusion model, we obtain (see Eqns (VIII.109)–(VIII.114) in [45])

$$J(q) = \alpha^{(q)} \frac{1}{bD} \operatorname{Re} \int du \frac{(J_{3/2}(u))^2}{u(u^2 - i\omega\tau_D)}, \quad (93)$$

where  $D$  is the diffusion coefficient of a radical,  $\alpha^{(0)} = (48/15)\pi$ ,  $\alpha^{(1)} = (8/15)\pi$ ,  $\alpha^{(2)} = (32/15)\pi$ ,  $\tau_D = b^2/(2D)$ , and  $J_{3/2}$  is the Bessel function. The integral in (93) has the form [54]

$$\int du \frac{(J_{3/2}(u))^2}{u(u^2 - i\omega\tau_D)} = \frac{i}{3\omega\tau_D} + \frac{\pi}{2\omega\tau_D} J_{3/2}((i\omega\tau_D)^{1/2}) H_{3/2}^{(1)}((i\omega\tau_D)^{1/2}), \quad (94)$$

where  $H_{3/2}^{(1)}$  is the Hankel function of the first kind.

For the closest approach of particles, the distance  $b$  between spins is of the order of a few angstroms. In liquids with the diffusion coefficient  $D \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , the time is  $\tau_D \sim 10^{-10} \text{ s}$ . The splitting  $\omega_k - \omega_n$  of the components of an EPR spectrum caused, for example, by the hyperfine interaction with magnetic nuclei usually does not exceed  $10^9 \text{ rad s}^{-1}$ . Therefore, spectral densities can be calculated assuming that  $\omega_k = \omega_n = \omega$  because  $|\omega_k - \omega_n|\tau_D \ll 1$  (where  $\omega$  is the mean frequency). This allows significantly simplifying kinetic equation (91), because kinetic equations can be assumed independent of subscripts  $k$  and  $n$ :

$$\begin{aligned} \frac{\partial M_{k-}}{\partial t} &= -i\omega_k M_{k-} - \frac{M_{k-}}{T_2} - \frac{M_{k-}}{T_{2d-d}} - \varphi_k \sum \frac{M_{n-}}{T'_{2d-d}}, \\ \frac{\partial M_{kz}}{\partial t} &= -\frac{M_{kz} - M_{k0}}{T_1} - \frac{M_{kz}}{T_{1d-d}} - \varphi_k \sum \frac{M_{nz}}{T'_{1d-d}}, \\ \frac{1}{T_{2d-d}} &= \frac{1}{8} \gamma^4 \hbar^2 C \left[ \frac{5}{4} J^{(0)}(0) + \frac{27}{2} J^{(1)}(\omega) + \frac{9}{4} J^{(2)}(2\omega) \right], \\ \frac{1}{T'_{2d-d}} &= \frac{1}{8} \gamma^4 \hbar^2 C [J^{(0)}(0) + 9J^{(1)}(\omega)], \\ \frac{1}{T_{1d-d}} &= \frac{1}{16} \gamma^4 \hbar^2 C [J^{(0)}(0) + 18J^{(1)}(\omega) + 9J^{(2)}(2\omega)], \\ \frac{1}{T'_{1d-d}} &= \frac{1}{16} \gamma^4 \hbar^2 C [-J^{(0)}(0) + 9J^{(2)}(2\omega)]. \end{aligned} \quad (95)$$

### 3.3 Kinetic equations for typical EPR experiments

For further applications, we write kinetic equations (95) for typical frequencies of EPR experiments. From Eqn (94), we obtain

$$\begin{aligned} J^{(q)}(\omega) &\approx \alpha^{(q)} \frac{2\tau_D}{b^3} \left[ \frac{2}{15} - \frac{1}{9\sqrt{2}} (\omega\tau_D)^{1/2} \right], \quad \omega\tau_D < 1, \\ J^{(q)}(\omega) &\approx \alpha^{(q)} \frac{1}{\sqrt{2}b^3} \frac{1}{\omega(\omega\tau_D)^{1/2}} \left( 1 - \frac{1}{\omega\tau_D} \right), \quad \omega\tau_D > 1, \end{aligned} \quad (96)$$

where  $\omega$  is the mean spin frequency. Resonance frequencies in EPR experiments are usually  $\omega \gtrsim 10^{11} \text{ rad s}^{-1}$ , and therefore the condition  $\omega\tau_D > 1$  is satisfied.

Substituting (96) in (95), we can express kinetic equations (95) in terms of a single independent parameter:

$$T_{d-d} = \left( \frac{2\pi}{75} \gamma^4 \hbar^2 C \frac{\tau_D}{b^3} \right)^{-1}, \quad (97)$$

$$\begin{aligned} \frac{1}{T_{2d-d}} &\equiv \frac{1}{T_{d-dsd}} \approx \frac{9}{T_{d-d}}, \quad \frac{1}{T'_{2d-d}} \equiv \frac{1}{T_{d-dset}} \approx \frac{4}{T_{d-d}}, \\ \frac{1}{T_{1d-d}} &\equiv \frac{1}{T_{d-drp}} \approx \frac{2}{T_{d-d}}, \quad -\frac{1}{T'_{1d-d}} \equiv \frac{1}{T_{d-dpt}} \approx \frac{2}{T_{d-d}}, \end{aligned}$$

Subscripts indicate processes characterizing the corresponding time.  $T_{d-drp}$  characterizes the decrease in the longitudinal magnetization (the population difference of spin levels) of a selected particle caused by the dipole–dipole interaction with all spins in the system. We can say that  $T_{d-drp}$  characterizes the relaxation of the longitudinal spin polarization,  $T_{d-dpt}$  characterizes the longitudinal polarization transfer from all spins of the system to the selected spin,  $T_{d-dset}$  corresponds to the spin coherence transfer from all spins to the selected spin, and  $T_{d-dsd}$  is the characteristic decoherence time of the selected spin induced by the dipole–dipole interaction with all spins in the system. Kinetic parameters (95) and (97) are inversely proportional to the diffusion coefficient of spin probes.

Thus, in the limit case  $\omega\tau_D \gg 1$  typical for EPR experiments, kinetic equations (91) reduce to the simpler equations

$$\begin{aligned} \frac{\partial M_{k-}}{\partial t} &= -i\omega_k M_{k-} - \frac{M_{k-}}{T_2} - \frac{5}{T_{d-d}} M_{k-} - \varphi_k \frac{4}{T_{d-d}} M_{-}, \\ \frac{\partial M_{kz}}{\partial t} &= -\frac{M_{kz} - M_{k0}}{T_1} - \frac{2}{T_{d-d}} M_{kz} + \varphi_k \frac{2}{T_{d-d}} M_z, \end{aligned} \quad (98)$$

$$M_{-} \equiv \sum M_{n-}, \quad M_z \equiv \sum M_{nz}.$$

The two underlined terms in these equations deserve attention. First, the underlined term in the equation for the  $z$  component of the magnetization has the same sign as the corresponding term in the case of spin exchange (see, e.g., (74)). It is known that the longitudinal polarization transfer for nuclear spins due to dipole–dipole and scalar interaction occurs with the opposite sign (see Eqns (VIII.88a), (VIII.128) in [45]). This is explained by the fact that in the case of electron spins, the longitudinal polarization transfer is mainly determined by the contribution from flip-flop transitions, while in the case of nuclear spins, the contributions of flip-flip or flop-flop transitions dominate. Second, the equation for the transverse components of the magnetization contains the added underlined term, which had been erroneously discarded (see Eqns (VIII, 89) in [45] and (2.19) in [55]), which resulted in ignoring the spin coherence transfer caused by the dipole–dipole interaction simultaneously with its transfer due to the exchange interaction. A comparison of (98) and (74) shows that contributions from the exchange and dipole–dipole interactions to the longitudinal spin polarization transfer are added, whereas their contributions to the spin coherence transfer are subtracted.

We note that the spin–lattice relaxation rate  $1/T_1$  in Eqns (98) contains a contribution from the dipole–dipole interaction, i.e.,  $1/T_1 = 1/T_{10} + 1/T_{1d}$ , where  $1/T_{1d} = (9/8)\gamma^4 \hbar^2 C [J^{(1)}(\omega) + J^{(2)}(2\omega)]$  (see (95)). Here,  $T_{10}$  is the spin–lattice relaxation time of an isolated paramagnetic particle.

The correct treatment of the contribution from the dipole–dipole interaction to the spin coherence transfer is one of the key features of a new paradigm of spin exchange between paramagnetic particles in solutions.

#### 4. Manifestation of the spin exchange and dipole–dipole interaction in the shape of EPR spectra of free radicals

Taking into account that the most popular spin probes are nitroxyl radicals, we now consider manifestations of the spin exchange in EPR spectra using the example of nitroxyl radicals. Of course, our treatment can also be used to study bimolecular collisions of other paramagnetic particles.

The hyperfine interaction (HFI) with magnetic nuclei splits spin energy levels; as a result, the EPR spectra of radicals have a hyperfine structure (HFS). Each HFS spectral component corresponds to a certain ‘configuration’ of magnetic nuclear spins. The EPR spectrum of nitroxyl radicals has two HFS components for the  $^{15}\text{N}$  isotope and three components for the  $^{14}\text{N}$  isotope caused by the HFI with the nitrogen nucleus, because the nuclear spin projection on the external constant magnetic field direction can have two values,  $+1/2$  and  $-1/2$ , for the  $^{15}\text{N}$  isotope (the nuclear spin  $I = 1/2$ ) and three values, 1, 0, and  $-1$ , for the  $^{14}\text{N}$  isotope (nuclear spin  $I = 1$ ). Each nitrogen HFI spectral component consists of a number of lines caused by the HFI with protons. EPR experiments are performed in quite strong magnetic fields, such that the HFI of the electron, spin  $S$ , and the nuclear spin  $I$ , can be described by the spin Hamiltonian  $H_{\text{HFI}} = \hbar a S_z I_z$ , where  $a$  is the HFI constant.

In the case of nitroxyl radicals at relatively low concentrations, an exchange narrowing of the EPR spectrum components corresponding to the different projections of the nitrogen nuclear spin occurs. This happens when the spin exchange rate  $K_{\text{ex}}C$  becomes comparable to the broadening of these components due to the HFI with protons. At higher radical concentrations, when the spin exchange rate becomes comparable to the HFI constant with the nitrogen nucleus, the exchange narrowing of the total EPR spectrum occurs. This complicates the determination of the spin exchange rate from the shape of EPR spectra but at the same time creates additional possibilities (see [11]).

##### 4.1 General solution for the shape of EPR spectra for radicals in solutions

In EPR experiments, a constant magnetic field  $B_0$  is commonly used and a linearly polarized alternating magnetic field  $B_x = 2B_1 \cos(\omega t) = B_1 [\exp(-i\omega t) + \exp(i\omega t)]$  is applied with a frequency  $\omega$  and amplitude  $2B_1$ . The resonance response produces only one of the rotating components of this field. Retaining only one component  $B_1$  of the field and passing to a coordinate system rotating with the frequency  $\omega$ , we obtain a system of kinetic equations for the partial magnetizations of spins related to different hyperfine components of the EPR spectrum (see (74), (95), (97), (98)):

$$\begin{aligned} \frac{\partial M_{k-}}{\partial t} &= -i(\omega_k + \delta_k - \omega)M_{k-} \\ &\quad - \frac{M_{k-}}{T_{2k}} - \left( K_{\text{ex}}C + \frac{1}{T_{\text{d-dsd}}} \right) M_{k-} \\ &\quad + \varphi_k \left( K_{\text{ex}}C - \frac{1}{T_{\text{d-dsct}}} \right) M_{-} - i\gamma B_1 M_{kz}, \\ \frac{\partial M_{kz}}{\partial t} &= -\gamma B_1 M_{ky} - \frac{M_{kz} - M_{k0}}{T_1} - \left( K_{\text{ex}}C + \frac{1}{T_{\text{d-drp}}} \right) M_{kz} \\ &\quad + \varphi_k \left( K_{\text{ex}}C + \frac{1}{T_{\text{d-dpt}}} \right) M_z, \end{aligned}$$

$$M_{-} \equiv M_x - iM_y \equiv \sum M_{n-}, \quad M_z \equiv \sum M_{nz}. \quad (99)$$

It is interesting that the spin coherence transfer rate  $V_{\text{sct}} = K_{\text{ex}}C - 1/T_{\text{d-dsct}}$  in (99) can vanish for a certain diffusion coefficient of the spin probe.

EPR spectra measured in experiments are proportional to the stationary value of the magnetization projection  $M_y$  on the  $y$  axis. It can be found by equating the right-hand sides of (99) to zero.

We consider the solutions of these equations in the case of weak fields  $B_1$ , when saturation effects can be ignored, assuming that  $M_{kz} \approx M_{k0} = \varphi_k M_0$ . As a result, we obtain the transverse magnetization of the system [11, 12]:

$$\begin{aligned} M_{-} &= i\gamma B_1 M_0 \frac{G(\omega)}{1 + (K_{\text{ex}}C - 1/T_{\text{d-dsct}})G(\omega)}, \\ G(\omega) &= \sum_k \frac{\varphi_k}{-i(\omega_k + \delta_k - \omega) - 1/T_{2k} - (K_{\text{ex}}C + 1/T_{\text{d-dsd}})}, \end{aligned} \quad (100)$$

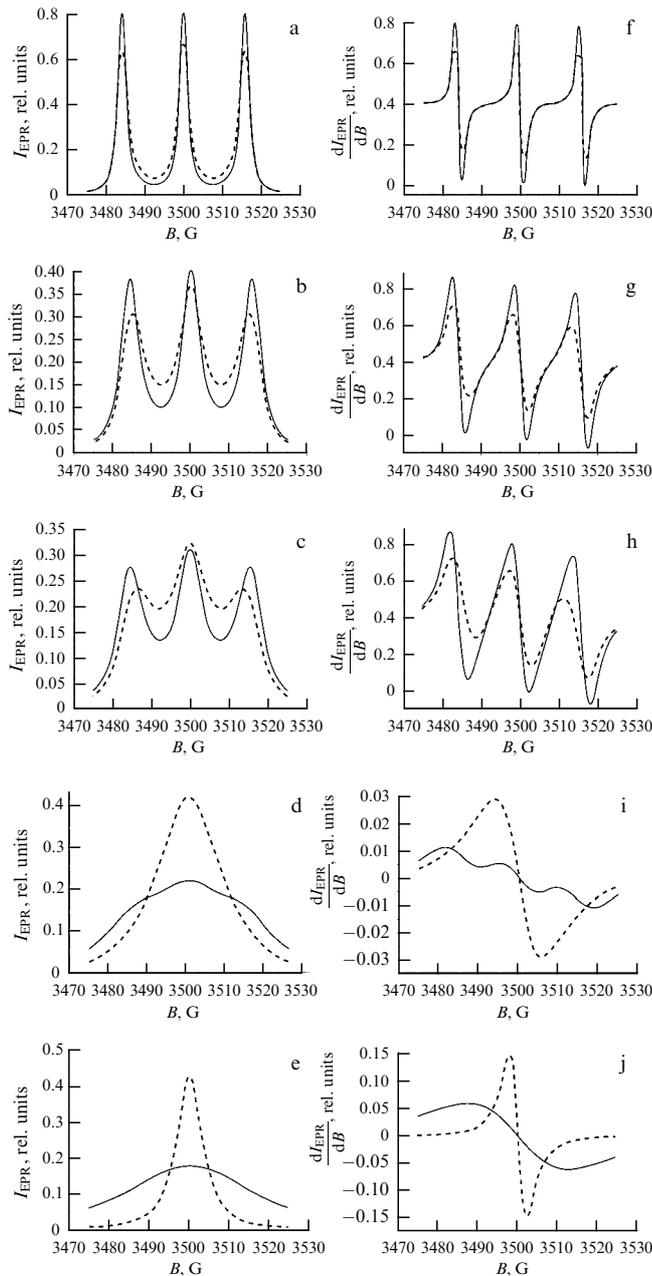
where the magnetization projection is  $M_y = -\text{Im } M_{-}$ .

The influence of the spin coherence transfer on the shape of the spectrum is illustrated in Fig. 3, where the EPR spectra of a model nitroxyl radical calculated using (100) are presented. It is assumed that an unpaired electron interacts with one magnetic nucleus  $^{14}\text{N}$  with the spin  $I = 1$ . This gives three hyperfine nitrogen components in the EPR spectrum at low radical concentrations. We also assume that each hyperfine nitrogen component has the unresolved hyperfine structure due to interaction with protons, and the inhomogeneous broadening of each nitrogen component of the spectrum can be described by a Gaussian distribution with dispersion  $\sigma$ .

We can see from Fig. 3 that the shape of the spectrum depends very strongly on the radical concentration. At low concentrations, all spectral lines broaden and extreme components shift to the center of the spectrum. At high radical concentrations, the entire spectrum collapses into one homogeneously broadened line at the center of gravity of the spectrum. If the contribution of the dipole–dipole interaction is negligibly small, at high radical concentrations, the spectrum transforms into one narrow line (see the behavior of dashed curves with changing concentration). This effect is called the exchange spectral narrowing. But if, along with the spin exchange, the quantum coherence kinetics are also determined by the dipole–dipole interaction, then the EPR spectrum broadens at high concentrations due to the dipole–dipole interaction of spins, although the collapse of all spectral lines into one homogeneously broadened line occurs (cf. spectral widths in Figs 3e,j at the concentration  $C = 500 \text{ mM l}^{-1}$ ). The collapse of the spectrum sets in when the spin-coherence transfer rate becomes comparable to the ‘nitrogen’ splitting of the spectrum. In this case, the EPR spectrum is described by a Lorentzian with the width given by [11, 22]

$$\frac{1}{T_{2\text{eff}}} \equiv \frac{1}{T_{\text{d-dsd}}} + \frac{1}{T_{\text{d-dsct}}} + \frac{2a_{\text{N}}^2}{3(K_{\text{ex}}C - 1/T_{\text{d-dsct}})} + \frac{1}{T_2}. \quad (101)$$

Curves in Figs 3b,c,g,h show that in the slow spin exchange region, the extreme components of the spectrum are asymmetric and are the sum of a symmetric absorption line and an antisymmetric dispersion line. This conclusion is



**Figure 3.** (a–e) EPR spectra calculated by expressions (100) and (f–j) their derivatives with respect to the magnetic field induction for  $^{14}\text{N}$  nitroxyl radicals at different radical concentrations. Parameters used in calculations: HFI constant  $a_{\text{N}} = 16$  G,  $g = 2$ ,  $\sigma = 0.12$  G $^2$ ,  $1/T_2 = 0.2$  G. Dashed curves are calculated ignoring the dipole–dipole interaction,  $K_{\text{ex}} = 0.1$  G l mM $^{-1}$ ,  $1/T_{\text{d-d,sd}} = 0$ . Solid curves are calculated taking the dipole–dipole interaction into account,  $K_{\text{ex}} = 0.05$  G l mM $^{-1}$ ,  $1/T_{\text{d-d,sd}} = 0.011$  G l mM $^{-1}$ ,  $1/T_{\text{d-d,set}} = 0.009$  G l mM $^{-1}$ . Because frequencies in EPR spectroscopy are measured in gauss, the rates of spin processes are presented in gauss. 1 G corresponds to the circular frequency  $1.76 \times 10^7$  rad s $^{-1}$ .

proved in Section 4.2 (see Eqn (105) and Figs 5 and 6). The asymmetry of extreme lines can be demonstrated by the fact that derivatives at the maximum-slope points for extreme spectral components do not coincide (see curves in Figs 3a–c, f–h). In fact, the derivatives of spectral components at the maximum-slope points can also differ because of the overlap of the wings of extreme spectral components with the central component. However, the asymmetry of extreme components is greater than could be expected due to the simple overlap of

the adjacent spectral components. The mixed shape of lines in the EPR spectrum caused by the spin coherence transfer has been theoretically predicted for quite a long time [12, 13], but this was not studied experimentally for a long time. We note that the deviation of the line shape from a Lorentzian due to the spin exchange has already been observed for the aqueous solution of  $\text{K}_2(\text{SO}_3)_2\text{NO}$ . The conclusive experimental demonstration of the mixed shape of lines and analysis of the dispersion contribution to the shape of the EPR spectrum in the case of spin exchange are presented in a number of papers (see, e.g., [11, 15, 16, 57]). When a spectral component has the mixed shape (absorption + dispersion), the maximum-slope points of the component on the left and on the right are located at different heights. Therefore, the frequency distance between the maximum-slope points does not directly specify the width of the spectral component, as in the case of symmetric absorption lines.

The fact that resonance lines in the region of slow spin-coherence transfer have a mixed shape (absorption + dispersion) is the principal difference between the new spin-exchange paradigm and the existing paradigm.

#### 4.2 New look at the role of spin coherence transfer.

##### Collective evolution modes of the system spin coherence

Equations (100) are quite convenient for computer studies of the influence of spin exchange and dipole–dipole interaction on the shape of the EPR spectrum. However, such an approach does not allow completely elucidating the physical nature of the spectral transformations observed (see Fig. 3).

A different approach exists for better understanding the physics of the relevant processes. This approach is based on finding the collective independent modes of the quantum coherence kinetics [10, 12, 13]. For this, we write system of equations (99) in a different form. We consider the case of a weak field  $B_1$ , when saturation effects can be disregarded, and set  $M_{kz} \approx M_{k0} = \varphi_k M_0$ . We introduce vectors  $\mathbf{M}_-$  and  $\mathbf{M}_0$  with projections  $M_{k-}$  and  $\varphi_k M_0$ . We construct the matrix  $L$  from coefficients of system of equations (99). Equations (99) can be written in the form

$$L\mathbf{M}_- - i\gamma B_1 \mathbf{M}_0 = 0. \quad (102)$$

We can find the eigenvalues  $\{\lambda_k\}$  and eigenvectors of the evolution operator  $L$  by solving the equation

$$LX_k = \lambda_k X_k. \quad (103)$$

The eigenvectors of  $L$  are superpositions of the transverse magnetizations  $M_{k-}$  of spins belonging to different components of the EPR spectrum. In fact, these eigenvectors are independent collective modes of the evolution of quantum coherences of the system. Each collective mode can in principle give a resonance response to the external action. The observed absorption spectrum is the sum of independent contributions of the resonance responses of collective modes to the action of an external alternating field. It has not yet been found how the external field excites each collective mode [10]. To do this, it is necessary to find the matrix  $U$  performing a similarity transformation from the matrix  $L$  to the diagonal matrix  $ULU^{-1}$  [58]. Therefore, it is necessary to transform the vector  $\mathbf{F}$  describing the action of the external perturbation,  $\mathbf{F} \equiv i\gamma B_1 \mathbf{M}_0$  (see (102)). After the transformation, this vector becomes  $\mathbf{F}^* = i\gamma B_1 U\mathbf{M}_0$ . The vector  $\mathbf{M}_-$  is transformed similarly under the transition to collective modes,  $\mathbf{M}_-^* = U\mathbf{M}_-$ . As a result, the contribution of collective modes to the observed spectrum is determined by

the quantities

$$M_{k-}^* = \frac{F_k^*}{\lambda_k}. \quad (104)$$

The resonance effect is observed when  $|\lambda_k|$  takes the minimal value. We note that  $\lambda_k$  has the form  $\lambda_k = -i(\Omega_k - \omega) - \Delta\Omega_k$ . The imaginary part of  $\lambda_k$  determines the resonance frequency  $\Omega_k$ , and the real part specifies the width of the resonance. The contribution of collective modes to the spectrum is determined by the components of the vector  $\mathbf{F}^*$ . It was shown in [10, 12, 13] that in the general case,  $F_k^* = c_k + if_k$ . As a result, we obtain the contribution of an individual collective mode to the absorption spectrum in the form

$$J_k^* = -\text{Im } M_{k-}^* = \frac{f_k \Delta\Omega_k - c_k(\Omega_k - \omega)}{(\Omega_k - \omega)^2 + \Delta\Omega_k^2}. \quad (105)$$

It hence follows that in general, the resonance of a collective mode is a mixture of the Lorentzian absorption line and the Lorentzian dispersion line. The spectrum observed in experiment is

$$M_y = -\text{Im } M_- = -\text{Im } (UM_-^*) \quad (106)$$

and is a superposition of the  $J_k^*$  lines in (105). Thus, we have two identical representations of the spectrum observed in experiment: the first is the sum of independent collective modes (106), and the second is given by Eqn (100).

In the general case where the EPR spectrum consists of many components, this problem is solved only for the slow spin exchange, when the perturbation theory with the parameter

$$\frac{|K_{\text{ex sct}} C - 1/T_{2\text{d-d sct}}|}{\Delta\omega} < 1$$

can be applied (see (99), where  $\Delta\omega$  is the inhomogeneous width of the spectrum (see [11–13, 21, 22]). From Eqn (99) in the first-order perturbation theory, we obtain the contribution of the spin exchange and dipole–dipole interaction to the additional homogeneous broadening of the  $k$ th collective resonance. For example, in the case of the equivalent spin exchange, when  $\Delta\omega\tau_c < 1$ , the collective resonance linewidth is

$$\Delta\Omega_k = \frac{1}{T_{2\text{d-d sd}}} + \varphi_k \frac{1}{T_{2\text{d-d sct}}} + K_{\text{ex}}(1 - \varphi_k)C. \quad (107)$$

In the same situation in the second-order perturbation theory, we obtain the frequency shift of the  $k$ th collective resonance due to the spin exchange and dipole–dipole interaction:

$$\delta\omega_k = \varphi_k \left( K_{\text{ex}} C - \frac{1}{T_{2\text{d-d sct}}} \right)^2 \sum' \frac{\varphi_n}{\omega_n - \omega_k}, \quad (108)$$

where summation ranges  $n \neq k$ .

Equations (107) and (108) can be used, in principle, to find spin exchange rate constants if the broadening and shift of resonances depending on the spin concentration are known. However, the realization of this fundamental possibility is complicated by the fact that the mixed shape of lines and their overlap in expressions (107) and (108) have been ignored (see Section 5).

Attempts to describe the spin exchange contribution to the behavior of individual paramagnetic particles are being

made in the framework of the conventional paradigm. The new paradigm is based on the collective modes of spin motion that are formed during the spin coherence transfer from colliding partners. We can say that the ‘recoil in collisions’ (reaction in collisions in accordance with Newton’s third law) produces collective motion modes. For example, under exchange narrowing conditions in EPR experiments, some collective modes are not in fact excited.

### 4.3 Collective motion modes of spin coherence for model systems

**4.3.1 Two-frequency model.** To illustrate the formation of collective modes in the spin-coherence evolution in solutions of paramagnetic particles, we consider a simple system [10] representing a diluted solution of stable free radicals in which the unpaired electron interacts only with one magnetic nucleus  $^{15}\text{N}$ . The hyperfine interaction constant is  $a$ . The total ensemble of radicals can be divided into two subensembles with different nuclear spin projections on the direction of an external constant magnetic field. We assume that the coherence transfer is induced only by the equivalent spin exchange. We use this assumption only to simplify analytic expressions. The final conclusions depend essentially only on the presence of the spin coherence transfer. To calculate the shape of the EPR spectrum in the absence of saturation effects, it is necessary to find a stationary solution of Eqns (99). For the two-particle model under study, the coherence of spins belonging to two radical subensembles is described by the kinetic equations (cf. Eqns (99))

$$\begin{aligned} \frac{\partial M_{1-}}{\partial t} &= \left[ -i \left( \omega_0 + \frac{a}{2} - \omega \right) - \Gamma \right] M_{1-} \\ &\quad - VM_{1-} + VM_{2-} - \frac{i}{2} \omega_1 M_0, \\ \frac{\partial M_{2-}}{\partial t} &= \left[ -i \left( \omega_0 - \frac{a}{2} - \omega \right) - \Gamma \right] M_{2-} \\ &\quad - VM_{2-} + VM_{1-} - \frac{i}{2} \omega_1 M_0. \end{aligned} \quad (109)$$

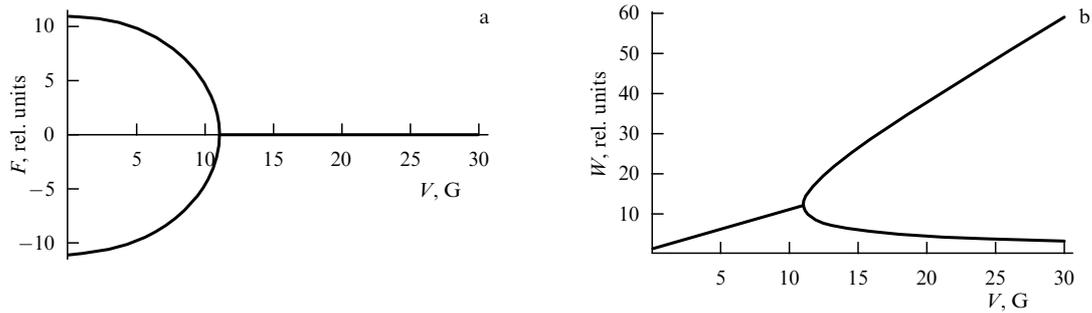
Here,  $\omega_0$  is the Zeeman frequency of the electron spins of radicals,  $\Gamma = 1/T_2$  is the spin decoherence rate determined by the interaction of spins with the medium, and  $\omega$  and  $\omega_1 = \gamma B_1$  are the carrier frequency and the Rabi frequency of the microwave field. We note that Eqns (109) are written in the coordinate system rotating at the frequency  $\omega$ . In the situation under study,  $V = K_{\text{ex}} C/2$ , where  $C$  is the concentration of all radicals and  $C/2$  is the concentration of radicals in each of the two subensembles with different nuclear spin projections. For the model system (109) under study, we have

$$L = \left\{ \left\{ -i \left( \omega_0 + \frac{a}{2} - \omega \right) - \Gamma - V, V \right\}, \right. \\ \left. \left\{ V, -i \left( \omega_0 - \frac{a}{2} - \omega \right) - \Gamma - V \right\} \right\}. \quad (110)$$

The eigenvalues of  $L$  are

$$\begin{aligned} \lambda_1 &= -i(\omega_0 - \omega) - \frac{R}{2} - \Gamma - V, \\ \lambda_2 &= -i(\omega_0 - \omega) + \frac{R}{2} - \Gamma - V, \end{aligned}$$

where  $R \equiv (-a^2 + 4V^2)^{1/2}$ .



**Figure 4.** (a) Dependence of the resonance frequencies of collective modes of the spin coherence evolution and (b) the width of these collective resonances on the spin coherence rate for the two-frequency model. Calculations are performed with the parameters  $a = 22$  G and  $\Gamma = 1$  G.

If the coherence transfer rate is negligibly small,  $V \approx 0$ , then the distance between two lines in the spectrum is equal to the HFI constant  $a$ . In the region  $2|V| < |a|$ , the line splitting in the spectrum is  $\text{Im } R = (a^2 - 4V^2)^{1/2} \approx a - 2V^2/a$ , which shows that the line splitting decreases and the lines approach each other with increasing the spin coherence transfer rate. In this case, both resonances have the same width, equal to  $V + \Gamma$ . Two frequencies (the imaginary parts of  $\lambda_1$  and  $\lambda_2$ ) coincide when the critical coherence transfer rate  $|V_c| = |a|/2$  is reached. In the region  $|V| \geq |a|/2$ , two resonances also exist. The frequencies of these resonances coincide, but they have different widths:  $\Delta\Omega_{\pm} \approx V + \Gamma \pm (1/2)R$ . When  $2|V| \gg |a|$ , the linewidths can be approximately written as  $\Delta\Omega_{\pm} \approx V + \Gamma \pm [V - a^2/(8V)]$ . One of the resonances is narrow,  $\Delta\Omega_{-} \approx \Gamma + a^2/(8V)$ , and its width decreases with increasing  $V$  as the spin concentration increases. This effect is well known as the exchange spectral narrowing [12, 13]. The other resonance has a greater width  $\Delta\Omega_{+} \approx 2V + \Gamma - a^2/(8V) \rightarrow 2V + \Gamma$ .

Thus, in the case of exchange narrowing, the spectrum consists of two lines with the same resonance frequency, but one of them is narrow and the other is broad. The eigenvalues of the operator  $L$  give information about the frequency and width of possible resonance excitations of the system. However, the shape of the resonance lines and the integrated strength of the resonance response of different collective modes depend on how the external field excites these collective modes, i.e., on the values of  $F_k^*$ . Calculations performed by the algorithm described above give the result

$$F^* = i\omega_1 X M_{\text{eq}} = \frac{i\omega_1}{2} M_0 \left\{ \frac{2V - ia - R}{2R}, \frac{2V - ia + R}{2R} \right\}. \quad (111)$$

Under conditions of exchange narrowing, with the coherence transfer rate  $V > a/2$ ,

$$F^* \approx \frac{i\omega_1}{2} M_0 \left\{ -\frac{ia}{4V}, 1 + \frac{ia}{4V} \right\} \rightarrow \frac{i\omega_1}{2} M_0 \{0, 1\}. \quad (112)$$

It hence follows that the external alternating magnetic field  $B_1$  efficiently excites only one of the collective modes of the spin coherence evolution. The detailed analysis in [10] shows that the external field excites a collective mode with a narrow resonance.

The changes in the shape of EPR spectra under changing the spin exchange rate are illustrated in the

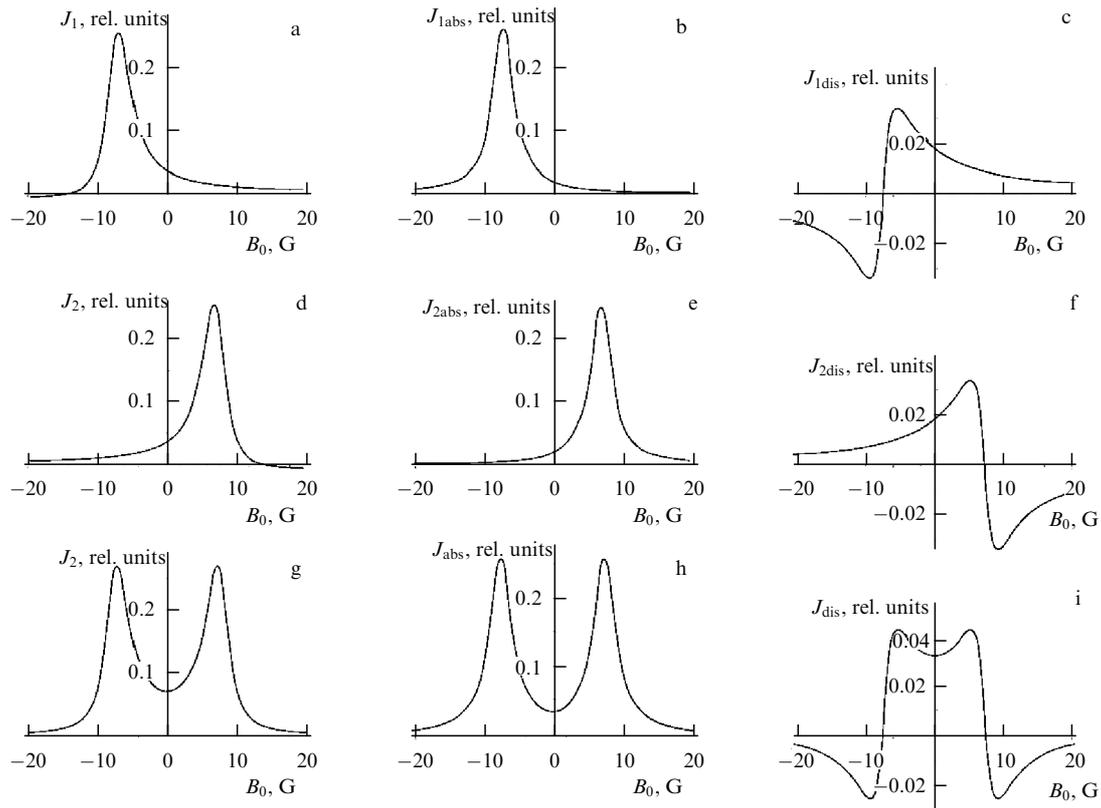
figures. We note that in EPR spectroscopy, hyperfine interaction constants, spectral line splittings, resonance frequencies, and line broadenings are measured in gauss. Therefore, we express the coherence transfer rate  $V$  also in gauss. To obtain the numerical value of  $V$  in  $[\text{rad s}^{-1}]$ , it is necessary to multiply the value of  $V$  in gauss by  $1.76 \times 10^7$ .

Figure 4 shows the dependences of the resonance frequency and width of collective modes of the quantum coherence evolution on the spin exchange rate. We can see that for  $V_c = a/2$ , a dramatic change occurs in the behavior of resonance frequencies and widths for collective modes.

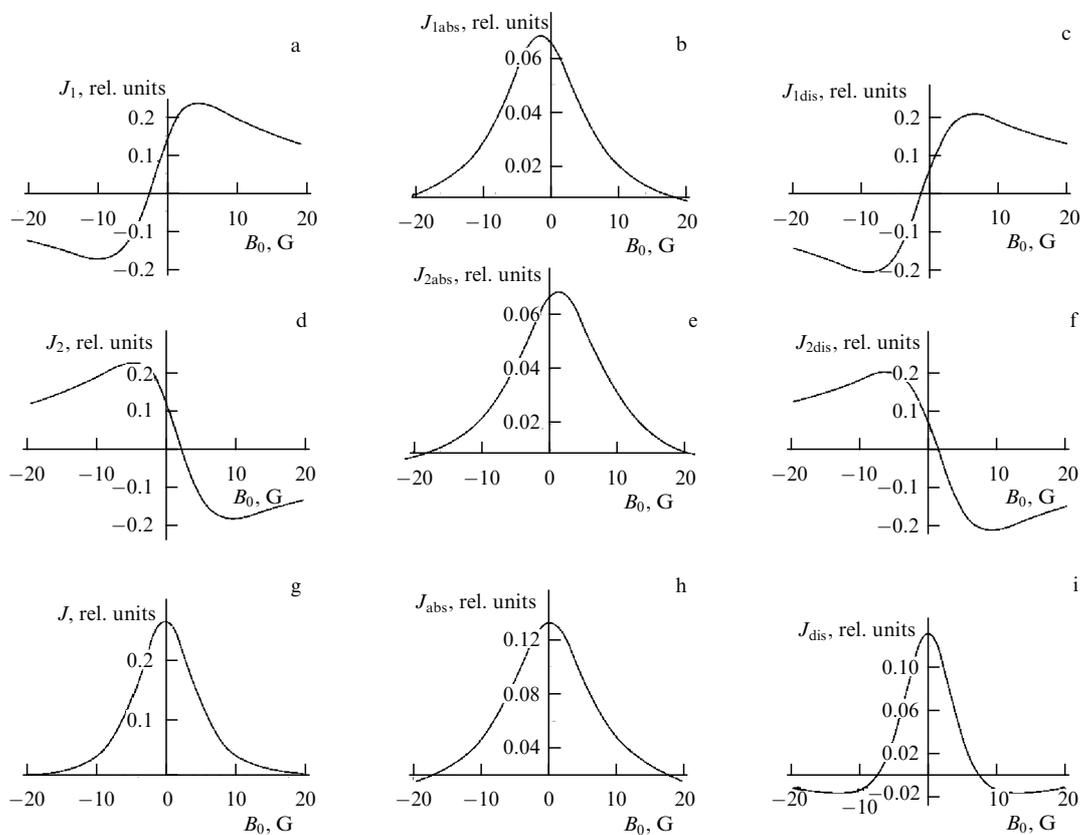
Figures 5a,d and 6a,d present the shapes of expected resonance lines  $J_1, J_2$  for each collective mode. These resonance lines have a mixed shape, being the sum of a Lorentzian absorption line and a Lorentzian dispersion line,  $J_k = J_{k,\text{abs}} + J_{k,\text{dis}}$ . Figures 5 and 6 clearly demonstrate the mixed shape of collective resonances. In the slow spin exchange region, the dispersion contribution is small (see Fig. 5); in the case of spectral narrowing, as  $|V| \rightarrow |a|/2$ , the absorption and dispersion contributions to the EPR spectrum equalize (see Fig. 6).

It follows from Fig. 7, that in the exchange narrowing case, the main contribution to the observed spectrum is made by one collective mode (the narrow resonance line), while the contribution of dispersion is absent. It is interesting that the collective mode with a broad resonance makes a contribution to the EPR spectrum with the negative sign (Fig. 7a). However, the integrated intensity of this line is very small.

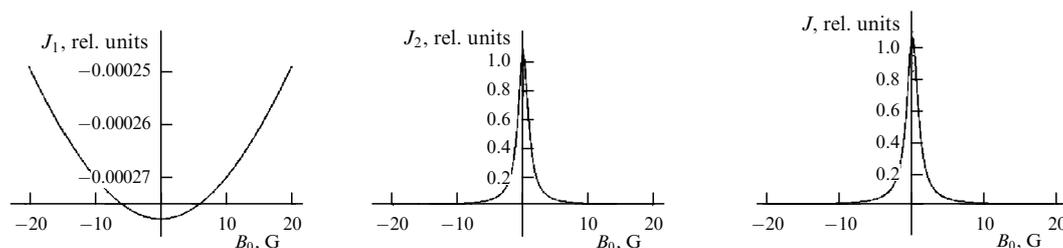
**4.3.2 Three-particle model.** In [10], the transformation of the spectrum was also analyzed in detail for a three-particle model. Such a situation is realized in EPR for  $^{14}\text{N}$  nitroxyl radicals. In general terms, the influence of the coherence transfer on the shape of the spectrum is similar to that in the two-particle case. However, differences also exist. We assume that in the absence of spin coherence transfer, resonances at frequencies  $\omega_1 = \omega_0 + a$ ,  $\omega_2 = \omega_0$ , and  $\omega_3 = \omega_0 - a$  are observed. It could be expected that in the case of rapid coherence transfer (exchange spectral narrowing), all three collective modes give a resonance at the mean frequency  $\omega_0$ . But this does not occur in reality (Fig. 8). We can see from Fig. 8 that in the three-particle model, the resonance frequencies of three collective modes do not become identical at any coherence transfer rate. But in EPR experiments at high spin exchange rates, only one of the resonances is excited.



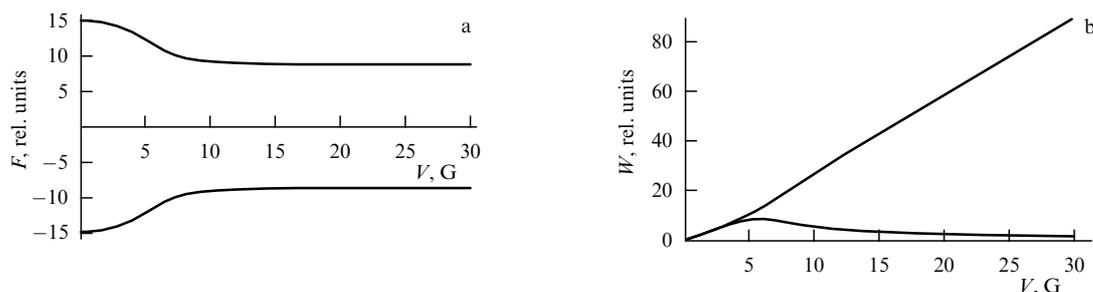
**Figure 5.** Contributions of collective modes with frequencies (a–c)  $\omega_0 + (a^2 - 4V^2)^{1/2}/2$  and (d–f)  $\omega_0 - (a^2 - 4V^2)^{1/2}/2$  to the EPR spectrum and (g–i) the total contribution of both collective modes,  $J = J_1 + J_2$ . Calculation parameters:  $a = 15$  G,  $V = 2$  G,  $\Gamma = 0$ .



**Figure 6.** Contributions of collective modes with frequencies (a–c)  $\omega_0 + (a^2 - 4V^2)^{1/2}/2$  and (d–f)  $\omega_0 - (a^2 - 4V^2)^{1/2}/2$  to the EPR spectrum and (g–i) the total contribution of both collective modes,  $J = J_1 + J_2$ . Calculation parameters:  $a = 15$  G,  $V = 7.4$  G,  $\Gamma = 0$ .



**Figure 7.** Contributions of collective modes of the spin coherence evolution to the observed EPR spectrum in the fast exchange case. Calculation parameters:  $a = 15$  G,  $V = 30$  G,  $\Gamma = 0$ .



**Figure 8.** Dependence of (a) the resonance frequencies of collective modes of the spin coherence evolution and (b) the width of these collective resonances on the spin coherence transfer rate  $V$  for the three-frequency model;  $a = 15$  G,  $\Gamma = 0$ .

## 5. How can the spin exchange rate be extracted from EPR spectra?

### 5.1 General observations

In EPR spectroscopy, the total contribution of two relaxation mechanisms dependent on the spin concentration is manifested. According to (100), concentration changes in the line shape are determined by the parameters  $W_{sd} = K_{ex}C + 1/T_{d-dsd}$  and  $V_{sct} = K_{ex}C - 1/T_{d-dsct}$ . The transformation of the spectrum is essentially determined by  $V_{sct}$ . The coherence transfer to a selected spin from colliding partners produces the mixed shape of lines in the slow-exchange region, the exchange narrowing effect. In the slow-exchange region, spectral lines are broadened (see (107)), shift to the center of gravity of the spectrum (see (108)), and are the sum of absorption and dispersion lines. In the fast spin exchange region, all spectral components merge into one homogeneously broadened line (101). In this case, the dipole–dipole interaction causes concentration broadening  $1/T_{d-dsd} + 1/T_{d-dsct} \sim C$ . This dipole spectral broadening exceeds the dipole–dipole contribution to the broadening of individual components of the spectrum in the slow spin exchange region, which is equal to  $1/T_{d-dsd} + \varphi_k/T_{d-dsct}$ . This observation correlates well with the known fact that the second moment of the dipole–dipole interaction between spins with the same resonance frequency is 9/4 times greater than in the case of different frequencies. In the exchange narrowing case, all the spins have the same resonance frequency. In the slow exchange case, the resonance frequencies are distributed and the spectrum is inhomogeneously broadened.

We note that for nonequivalent spin exchange during the collapse of the whole spectrum into one homogeneously broadened line, concentration broadening can be caused not only by the dipole–dipole but also by the exchange interaction because the spin decoherence rate constant  $K_{ex, sd}$  exceeds the spin coherence rate constant  $K_{ex, sct}$ .

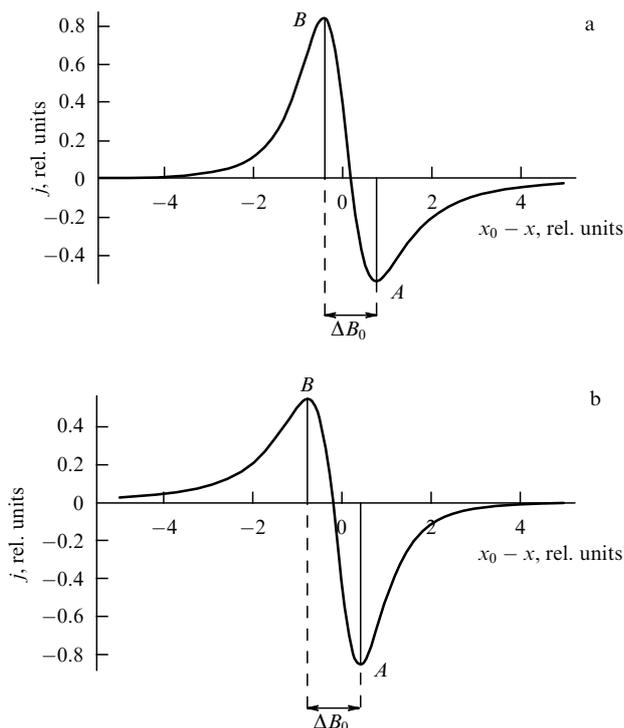
Manifestations of the spin exchange and dipole–dipole interaction of spins in the shape of the EPR spectrum mentioned above in principle allow determining the total spin decoherence and spin coherence transfer rates due to the exchange and dipole–dipole interactions. The contribution of the dipole–dipole interaction can be calculated using Eqns (97) and (98). The bimolecular spin exchange rates can be determined by subtracting the contribution of the dipole–dipole interaction from the total rates of the spin decoherence and spin coherence transfer found from experimental data.

Parameters of the spin decoherence and spin coherence transfer can be determined from the stationary solution of kinetic equations for spin density matrices (or spin magnetizations), the calculation of the spectrum and fitting the parameters in kinetic equations to obtain the best fit with experimental EPR spectra. This procedure is considerably simplified when the spin exchange can be considered equivalent, as expected for stable nitroxyl radicals. In this case, the spin exchange between free radicals is specified by a single rate constant  $K_{ex}$ , and the spectrum shape is described by compact expression (100). In the general case, the rate constants of the spin decoherence and spin coherence transfer due to the exchange interaction may not coincide, i.e., the spin exchange is not equivalent. Moreover, the spin exchange rates can be different for different components. The number of fitting parameters then increases, which, of course, complicates fitting (see, e.g., kinetic equation (91)).

In this connection, of interest are other approaches to estimating the rate constants of the spin decoherence and spin coherence transfer due to exchange interaction.

### 5.2 Method for determining the spin exchange rate constant from EPR spectra

A widespread method is based on the assumption of equivalent exchange. The line broadening in the slow exchange region is determined from the distance between the extrema of the derivative of the spectrum with respect to the



**Figure 9.** Derivatives of mixed spectral line shapes for (a)  $p = 0.4$  and (b)  $p = -0.4$ .

field (Fig. 9). As a result, based on experimental data and calculations of the contribution of the dipole–dipole interaction to the broadening of spectral lines, we can determine  $(1 - \varphi_k)K_{\text{ex}}C$  in (107) in the equivalent exchange case or  $K_{\text{exsd}}C - \varphi_k K_{\text{ex sct}}C$  in the nonequivalent exchange case. The resonance frequency and therefore the concentration frequency shift are determined from the constant magnetic field strength  $B_0$  at which the derivative of the spectrum with respect to the field vanishes (see Fig. 9).

Methods for determining the spin exchange rate constant are apparently quite reliable and have found wide applications [12, 13, 59]. However, new theoretical and experimental results have led to reconsidering these methods, except the one based on the concentration broadening of the exchange-narrowed EPR spectrum. In this case of a quite fast spin exchange, the spectrum transforms into a homogeneous Lorentzian line with the resonance frequency equal to the frequency of the center of gravity of the inhomogeneous spectrum at low spin concentrations. However, unfortunately, the exchange narrowing conditions are often difficult to achieve. Therefore, methods are needed for estimating spin-exchange kinetic parameters in the practically important slow spin exchange situation. The values of spin-exchange constants can be further refined by simulating spectra with the help of exact kinetic equations for partial magnetizations. In this case, the estimates obtained directly from experimental spectra can be used as good initial parameters for numerical simulations of spectra.

The above approaches to determining the concentration broadening of individual EPR lines and their resonance frequency were formulated by ignoring circumstances discussed in detail in Sections 2–4.

(1) The additional shift of resonance frequencies (e.g.,  $\delta_k$  in Eqn (108)) caused by the exchange interaction in

bimolecular collisions in the slow spin exchange region was ignored.

(2) The asymmetric shape of individual lines in the slow spin exchange region, when the concentration broadening of the lines occurs, was ignored. The lines are the sums of a symmetric Lorentzian absorption line and an asymmetric Lorentzian dispersion line with the same resonance frequency. The mixed line shape is given by the sum

$$j(x_0 - x) = \tau \left[ \frac{1}{1 + (x_0 - x)^2 \tau^2} + \frac{p(x_0 - x)\tau}{1 + (x_0 - x)^2 \tau^2} \right], \quad (113)$$

where  $x_0$  is the spin frequency,  $x$  is the microwave field frequency,  $\tau$  is the spin decoherence time determining the homogeneous width  $\Delta\Omega$  of the line under study, and  $1/\tau = \Delta\Omega$ . The parameter  $p$  in Eqn (113) specifies the dispersion contribution.

(3) The contribution of the dipole–dipole interaction to the spin coherence transfer from nonresonance spins to the separated spin was disregarded.

Ignoring the dipole–dipole interaction should systematically reduce the rate constant of the spin coherence transfer due to exchange interaction, because instead of the correct spin coherence transfer rate  $K_{\text{ex sct}} - 1/T_{2\text{d-d sct}}$ , the quantity  $K_{\text{ex sct}}$  is used, which is assumed equal to  $K_{\text{ex}}$ . Disregarding the dispersion contribution to the line shape, the position of the zero of the spectrum derivative does not give the correct resonance frequency (or the concentration frequency shift), and the interval between two external-field strengths determining the maximum and minimum values of the spectral line derivative does not coincide with the real width of the resonance. Therefore, the mixed shape of EPR lines is one of the most important characteristics of spectral lines caused by the spin coherence transfer. We let  $p$  denote the fraction of the dispersion contribution (see (113)). If  $p$  is known, the spin coherence transfer rate can be found. For example, for slow spin exchange in the second-order perturbation theory for the equivalent spin exchange, the expression

$$p_k = 2K_{\text{ex}}C \sum \frac{\varphi_n}{\omega_n - \omega_k} \quad (114)$$

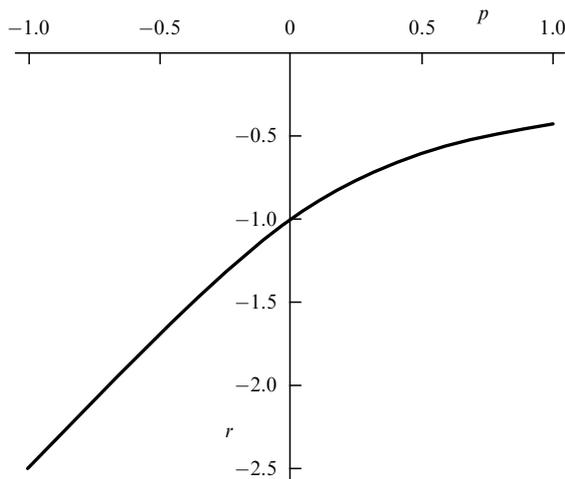
is obtained (see Eqns (1.81)–(1.87) in [12, 13] and also [11, 21, 22]). This means that  $p_k > 0$  for the low-field spectral components and  $p_k < 0$  for the high-field spectral components.

For arbitrary values of the spin coherence transfer rate, the exact value of the dispersion contribution  $p$  to the line shape was found in the simplest models with two or three resonance frequencies [10].

In [15], a new approach to determining the spin exchange rate from the shape of EPR spectra was proposed based on using the mixed shape of spectral components. First, the experimental spectrum is represented as the sum of symmetric absorption lines and antisymmetric dispersion lines, and the relative dispersion contribution  $p$  is found. We consider one of the approximate methods for estimating  $p$  from spectra [21]. The distance between the positions of the maximum and minimum of the derivative of a spectral line is (see Fig. 9) [21]

$$\Delta B_0 \approx (1.15 + 0.17p^2)\Delta\Omega, \quad (115)$$

where  $\Delta\Omega$  is the real width of the resonance. We note that expression (115) was derived by ignoring the possible overlap of adjacent lines.



**Figure 10.** Dependence of  $r = A/B$  (see Fig. 9) on the dispersion fraction  $p$  on the observed line.

Figure 9 presents the derivatives of the mixed line  $j(x)$  in (113) for two values of the dispersion fraction  $p$ . The maximum of  $j(x)$  gives the zero of its derivative (see Fig. 9). If  $p$  were zero, the maximum of (113) would be at  $x_0 = x$ . For  $p \neq 0$ , the maximum of (113) turns out to occur at [21]

$$x_0 = x + \frac{(1 + p^2)^{1/2} - 1}{p\tau}. \quad (116)$$

In Fig. 9,  $A$  and  $B$  are the minimal and maximal values of the derivative. In the slow spin exchange region,  $|p| < 1$  and the expression  $x_0 \approx x + p/(2\tau)$  turns out to be a good approximation [21]. Thus, due to the dispersion contribution, the maximum of line (113) shifts by  $p/(2\tau)$ .

The derivative of the spectrum observed in experiments allows finding the dispersion contribution directly from experiments. It was shown in [21] that the ratio  $r$  of the minimal value of the derivative of the spectrum ( $A$  in Fig. 9) to its maximal value ( $B$  in Fig. 9) depends only on  $p$ , i.e., is independent of the resonance frequency and width. The analytic expression for  $r = A/B$  is rather complicated [21], and therefore we present only the plot of this function in Fig. 10.

We note that the plot in Fig. 10 gives a one-to-one correspondence between two quantities. This plot can be treated as the dependence of the unknown quantity  $p$  on the parameter  $r$ , which can be easily found from the measured derivative of the EPR spectrum.

Thus, experimental and theoretical spin-exchange studies resulted in reconsidering the methods for determining the spin exchange rate from EPR spectra. The modern method involves the most important step in determining the dispersion fraction in the shape of spectral lines (see, e.g., [11]). To do this, for example, the ratio  $r$  of the minimal value of the line derivative to its maximal value is determined from experiments. The dispersion contribution  $p$  can be estimated from the plot in Fig. 10. More accurate methods for determining the parameter  $p$  from EPR spectra were also developed in [11]. Spin coherence transfer rates are then found from expressions (107) and (114). If the components of the EPR spectrum are resolved in a certain range of spin concentrations, then the spin exchange rate, i.e., the spin decoherence and spin coherence transfer due to exchange interaction, can be

found from measurements of the concentration dependence of the distance (115) between the maximum and minimum of the derivative of the spectrum with respect to the field. The spin coherence exchange transfer rate can be estimated from the concentration dependence of the position of a zero of the spectrum derivative using (116). These estimates of spin exchange rates can be used as initial values for simulations of spectra by solving the corresponding kinetic equations for particular paramagnetic particles. The state-of-the-art method for determining spin exchange rate constants in bimolecular collisions is considered in detail in [11, 16, 18, 57].

## 6. Prospects for using the spin exchange

The specific rate of bimolecular processes per unit concentration of particles is given by the rate constant  $K_{\text{ex}} = 4\pi r_{\text{ex}} D$ , where  $D$  is the mutual diffusion coefficient of two particles. The effective radii  $r_{\text{ex}}$  of the cross section of these processes depend on the exchange interaction parameters and kinematics of the relative motion of colliding particles.

The study of bimolecular processes caused by the exchange interaction of paramagnetic particles is of interest from several standpoints.

The kinematics of molecular motion in ‘simple’ media can be simulated sufficiently well. The values of  $r_{\text{ex}}$  found in EPR experiments in these systems can be used to determine parameters of the exchange integral: its value, the slope of its decay with distance between particles, and its anisotropy. This information about the exchange integral is useful for understanding the electron transfer reaction between molecules. The electron transfer is determined by the so-called resonance integral, which is proportional to the overlap integral of the electron wave functions, while the spin exchange is determined by the exchange integral, which is proportional to the square of the overlap integral of the electron wave functions. Experiments confirm the existence of a correlation between the radii of the spin exchange cross section and the intermolecular electron transfer [12, 13].

The spin exchange is also of interest in and of itself. The example of positronium quenching by paramagnetic particles due to their exchange interaction in collisions is presented in Section 2.3.4. A paramagnetic particle accelerates orthopositronium quenching. This process can be regarded as an example of the spin catalysis of the ortho–para positronium conversion. Other examples of spin catalysis can also be presented. Due to the exchange interaction, paramagnetic particles can accelerate the recombination of radical pairs in solutions [5, 6], accelerate the recombination of electron–hole pairs in semiconductors, and change the photocurrent density in molecular crystals because the spin exchange with a paramagnetic addition can change the spin multiplicity of excitons [60] and the polarization of luminescence from excited triplet states.

At present, the application of paramagnetic particles as spin probes is attracting special interest. Spin exchange is used as a model process for studying bimolecular collisions in complex biological systems and in polymer matrices (see reviews [59–61]). The study of spin exchange gives information on electrostatic interactions in bimolecular collisions of charged molecules in electrolytes. Spin exchange is used to determine the local concentration of paramagnetic particles in complex systems. For example, radiation therapy requires information on the concentration of oxygen molecules in certain parts of the body. Collisions of spin probes with

oxygen broaden the EPR lines of the probe. The concentration of oxygen molecules can be found from the EPR line broadening with the help of theoretical calculations of the effective radius of the spin exchange of the probe with oxygen. This method for measuring the concentration of paramagnetic particles is successfully used in oximetry [61–63].

Interest in studies of the spin exchange in solutions increases with the development of chemical technologies of attaching spin labels to molecules. Chemists have developed technologies for site-directed spin labeling. Site-directed spin labeling is of special interest for applications in biologically important molecular processes (see, e.g., [64, 65]).

To realize the potential of spin-labeled molecules for studying the molecular mechanisms of biochemical reactions, it is necessary to have suitable physical methods for investigations of bimolecular processes. In particular, an important molecular kinetic parameter is the frequency of bimolecular collisions. In complex systems, this frequency is determined by using the bimolecular spin exchange as the model process. Appropriate spin probes with known characteristics must be selected. For example, the parameters of the exchange integral must be known. To obtain information about the exchange integral for two colliding particles, the spin exchange is studied in ‘simple’ media, for example, in low-molecular solutions with a well-known viscosity, which do not exhibit any specific interaction with dissolved paramagnetic particles. Examples of such systems are stable nitroxyl radicals [59, 65]. Information about the exchange integral between specified paramagnetic particles obtained in this way is used to study bimolecular collisions in ‘complex’ media.

The analysis performed in this review shows that the state-of-the-art spin-exchange theory allows calculating the spin exchange rate and analyzing its dependence on molecular kinetic parameters of systems under study and the interaction parameters of spin labels. Methods for determining the spin exchange frequency from EPR spectra have also been developed.

Thus, we can assert that the state-of-the-art bimolecular spin exchange theory for diluted solutions and EPR spectroscopy create good foundations for the further development and application of the spin probe method in molecular biology and medicine.

## 7. Conclusions.

### Shift in the spin exchange paradigm

During the 50 years of studies of spin exchange in bimolecular collisions, our concepts have radically changed. The existing, in fact phenomenological, paradigm has been replaced by a new one. Its main differences from the previous paradigm can be summarized as follows.

The new paradigm distinguishes at least three different spin exchange processes: spin decoherence, spin coherence transfer, and spin excitation energy transfer. The existing paradigm assumed that all these elementary processes occur at the same rate.

The new paradigm distinguishes equivalent and non-equivalent spin exchanges. The nonequivalent spin exchange appears due to the presence of spin-dependent interactions in individual paramagnetic particles. Even if these interactions are a few orders of magnitude weaker than the exchange interaction, they can fundamentally change the result of collisions between paramagnetic particles. The existing

paradigm erroneously neglected the spin coherence transfer due to the dipole–dipole interaction.

Unlike the earlier paradigm, the new paradigm describes paramagnetic relaxation with the help of collective modes of motion of quantum spin coherence in solution. These collective modes appear exclusively due to the quantum coherence transfer during spin collisions. The resonance line of each collective mode has a mixed shape (absorption + dispersion). There are ‘selection’ rules for exciting collective modes by an external alternating magnetic field. The new paradigm gives an entirely new picture of the exchange narrowing of EPR spectra.

The spin coherence transfer in strong microwave fields, when the saturation effect is observed, not only causes the line broadening of the collective mode in the EPR spectrum, as expected, but also results in a dependence of the resonance frequency on the field amplitude. In this case, collective ‘modes’ of the spin system and the microwave field—magnetic polaritons—are formed [66].

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