Spin Exchange Between Charged Paramagnetic Particles in Dilute Solutions

**Kev M. Salikhov · Aydar Ye. Mambetov ·
Marcel M. Bakirov · Iskander T. Khairuzhdinov ·
Ravil T. Galeev · Ruslan B. Zaripov · Barney L. Bales**

Abstract Kinetic equations for the spin density matrix which take into account binary collisions and a method of calculating the spin exchange effective radius have been generalized to the case of dilute solutions of charged paramagnetic particles. The effective radius of the spin exchange and rate constant of the bimolecular spin exchange between charged paramagnetic particles in solutions have been calculated numerically. Calculations have been performed under the assumption that the exchange interaction is isotropic and decays exponentially with the increase in the distance between radicals, and the solution has a given dielectric permittivity and Debye screening radius. Dependences of the spin exchange rate constant on the mutual diffusion coefficient, exchange and electrostatic interactions parameters have been found numerically. The theory has been applied to experimental results taken from the literature. The rate constant of the spin exchange between radicals of like charge found from the experiment and calculated within the developed theory are in good qualitative agreement.

K. M. Salikhov (✉) · A. Ye. Mambetov · M. M. Bakirov · I. T. Khairuzhdinov · R. T. Galeev ·
R. B. Zaripov
Kazan Physical-Technical Institute, Russian Academy of Sciences, Kazan, Russia
e-mail: salikhov@kfti.knc.ru

K. M. Salikhov
Kazan Federal University, Kazan, Russia

B. L. Bales
Department of Physics and Astronomy, California State University at Northridge and the Center for
Supramolecular Studies, Stockton, USA

1 Introduction

1.1 Current Paradigm in the Spin Exchange Theory

Binary collisions of molecules in dilute solutions determine the rate of many physical, chemical and biochemical processes (see, e.g., [1, 2]). For example, the study of collisions of substrate molecules with the active regions of enzyme can make it possible to determine the extent of accessibility of the active catalytic enzyme center for drugs, etc.

The attention of scientists has been permanently focused on theoretical and experimental studies of bimolecular collisions.

The theory of bimolecular collisions in condensed matter is elaborated rather well for neutral (non-charged) molecules. The frequency of bimolecular collisions was calculated for the first time by Smoluchowski [3]. He considered a dilute solution of molecules assuming them to be solid spheres with given radii moving according to the model of continuous diffusion with a given diffusion coefficient. He obtained a well known result for the frequency of binary collisions of a selected molecule A with molecules B,

$$Z_{A0} = 4\pi(r_A + r_B)(D_A + D_B)C_B = 4\pi r_0 D_{AB} C_B. \tag{1}$$

In this equation r_A and r_B are radii of spheres representing molecules A and B, and D_A and D_B are diffusion coefficients of molecules-spheres A and B, respectively, C_B is the concentration of molecules B. We call the quantity $r_0 = r_A + r_B$ as the collision radius or the distance of the closest approach of molecules.

Equation (1) was derived under the assumption that at the first contact of spheres they stick together and "drop out of the game". Thus, Smoluchowski [3] did not consider re-encounters of the same pair of molecules A and B ([4]; see discussion of this problem in [5]). Therefore, Eq. (1) gives only the frequency of the first collisions of the selected molecule A with different molecules B.

It was shown in [4] that in condensed matter, two molecules approaching the distance r_0 may re-encounter (repeatedly approach) at the same distance after some diffusion walk. To illustrate the role of re-encounters in the bimolecular process, let us present the results for a simple phenomenological model. Let us denote the probability that two molecules re-encounter at the distance r_0 as p_r. This probability is determined by the kinematics of the molecular diffusion, namely, the mean displacement length of molecules in the elementary diffusion act and the size of molecules [5]. The total probability of all re-encounters is $q = p_r + p_r^2 + p_r^3 + \cdots = p_r/(1 - p_r)$. The total number of encounters of two selected molecules at the distance r_0 is $n = 1 + q = 1/(1 - p_r)$. Thus, the total collision frequency of the selected molecule A with molecules B should be

$$Z_{Af} = nZ_{A0} = 4\pi r_{eff} D_{AB} C_B. \tag{2}$$

We introduced an effective collision radius r_{eff}, which is $n = 1/(1 - p_r)$ times larger than the true collision radius of spheres, $r_{eff.} = nr_0 > r_0$. In addition to the first collisions with new molecules B, Eq. (2) takes into account all re-encounters of
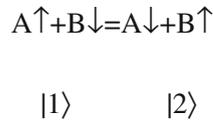
$$A{\uparrow}+B{\downarrow}=A{\downarrow}+B{\uparrow}$$

$$|1\rangle \qquad |2\rangle$$

Fig. 1 Scheme of the mutual flip-flop of spins of two paramagnetic particles with spin ½. *Arrows* indicate the orientations of spin moments of paramagnetic particles before and after the collision. Notations of the corresponding spin states of the pair, $|1\rangle$ and $|2\rangle$, are given below the scheme

the selected molecule A with the same molecule B. A set of all encounters of the same pair of molecules is called as a collision of two molecules.

The rate of a certain process occurring during bimolecular collisions is measured in the experiment. The frequency of bimolecular collisions can be, in principle, found from this rate. The measurement of the bimolecular spin exchange (see Fig. 1) is quite promising for solving this problem. On the one hand, the spin exchange rate can be found using methods of electron paramagnetic resonance (EPR), since this process is characteristically manifested in the shape of the EPR spectra [2]. On the other hand, this is a rather convenient process for a theoretical description. In fact, spin exchange (Fig. 1) is not associated with the additional activation as it takes place in the case of bimolecular chemical reactions or the reorganization of the medium during the electron exchange.

Exchange of spin states (Fig. 1) occurs under the action of the exchange interaction between paramagnetic particles A and B. Let us assume that the exchange interaction is switched on only in a very narrow layer δ between spheres with radii r_0 and $r_0 + \delta$. Let us denote the probability of the mutual flip-flop of spin moments during one collision as w_{ex}. In the interval $\{r_0, r_0 + \delta\}$ the exchange integral for the pair AB is J_0 and the average duration of one collision is τ_c. In this work we assume that the exchange integral does not depend on the mutual orientation of colliding paramagnetic particles. Note that the spin density of paramagnetic particles is not distributed uniformly, so that the exchange integral might depend on a mutual orientation of two colliding partners. The rotational diffusion of paramagnetic particles and their relative translational diffusion between re-encounters tend to average these anisotropic effects in the spin exchange. In the present paper, we do not consider this motif of anisotropy effects in spin exchange. More information about this subject can be found, e.g., in refs. [2, 6, 7]. For the model of the sudden switching of the exchange interaction between paramagnetic particles during the encounter, the probability of the mutual flip-flop of spins (Fig. 1) was calculated in a series of works [2, 8–10]:

$$w_{ex} = \frac{1}{2}\frac{J_0^2\tau_c^2}{1 + J_0^2\tau_c^2}. \tag{3}$$

After the first encounter of the pair A and B, the exchange of spin states according to Fig. 1 occurs with the probability w_{ex} and the spin states remain the same with the probability $1 - w_{ex}$. However, the spin exchange according to scheme Fig. 1 can also occur at the re-encounters of the pair. Re-encounters in the pair lead to the increase in the time τ_e, which colliding spins A and B spend in the

region $\{r_0, \ r_0 + \delta\}$ with the exchange interaction J_0. On average this time is $\tau_e = n\tau_c$. In this situation it seems reasonable to assume that the average probability of the spin exchange in one collision is given by expression (3) with the replacement of the average time of one encounter τ_c by the average summary duration of all encounters in one collision: $\tau_e = n\tau_c$. However, this assumption is justified only if in the intervals between re-encounters no spin evolution takes place, and the quantum coherence of the states of spins $|1\rangle$ and $|2\rangle$ is preserved. In the real situation, this condition is not fulfilled. Therefore in the general case, it is not possible to allow for the effect of all re-encounters by the simple substitution of the average time of one encounter by the average summary duration of all encounters $\tau_e = n\tau_c$ in Eq. (3).

To illustrate the effect of the spin decoherence in the intervals between subsequent re-encounters on the spin exchange efficiency, let us present the calculation of the probability of the spin exchange during a collision for the following phenomenological model. Let us denote the probability of the pair of spins to undergo the repeated contact as p_r. Suppose that in the interval between re-encounters the quantum coherence of states $|1\rangle$ and $|2\rangle$ (see Fig. 1) is destroyed, and to the moment of the beginning of the first and all subsequent re-encounters the state of the pair of colliding spins can be described completely by the populations of states $|1\rangle$ and $|2\rangle$. Of course, in the moment of an encounter the exchange interaction between spins forms the quantum coherence of states $|1\rangle$ and $|2\rangle$, so that in the moment of ending the encounter spins occur in the quantum coherent state of the superposition of states $|1\rangle$ and $|2\rangle$.

To calculate in the framework of the model described the total contribution of all re-encounters of a pair of spins A and B at the collision radius, let us introduce the matrix V of the probabilities of transitions between states $|1\rangle$ and $|2\rangle$ (see Fig. 1)

$$V = \begin{pmatrix} 1 - w_{ex} & w_{ex} \\ w_{ex} & 1 - w_{ex} \end{pmatrix}.$$

This matrix makes it possible to calculate the change of the populations of states $|1\rangle$ and $|2\rangle$ during the time of one encounter as a result of the coherent motion of two spins under the action of the exchange interaction.

Eigenvalues and eigen states of the matrix V are 1 and $1 - 2w_{ex}$, $|\psi_1\rangle = (|1\rangle + |2\rangle)/\sqrt{2}$ and $|\psi_2\rangle = (|1\rangle - |2\rangle)/\sqrt{2}$, respectively. On the basis of eigen states, the matrix V is

$$V_r = \begin{pmatrix} 1 & 0 \\ 0 & 1 - 2w_{ex} \end{pmatrix}. \tag{4}$$

On the same basis, the states of spins $\uparrow\downarrow$ and $\downarrow\uparrow$ are described by vectors $u_1 = \{1, 1\}/\sqrt{2}$ and $u_2 = \{1, -1\}/\sqrt{2}$. The probability that the spin exchange occurs as a result of the first encounter of two paramagnetic particles, after which these particles are separated in the volume of the solution not undergoing any re-encounters, is: $p_1 = (1 - p_r)\langle u_2|V_r|u_1\rangle$. The probability of the spin exchange as a result of the first encounter and one re-encounter is: $p_2 = (1 - p_r)$ $\langle u_2|V_r p_r V_r|u_1\rangle = (1 - p_r)\langle u_2|p_r V_r^2|u_1\rangle$. If k encounters occur, the probability of the spin exchange is $p_k = (1 - p_r)\langle u_2|p_r^{k-1}V_r^k|u_1\rangle$.

Summing the contribution of all possible implementations of re-encounters, we find the probability of the mutual flip-flop of spins of the pair of paramagnetic particles A and B in one collision:

$$p_{\mathrm{t}} = \sum p_k = \frac{n w_{\mathrm{ex}}}{1 + 2(n-1)w_{\mathrm{ex}}} = \frac{1}{2} \frac{n J_0^2 \tau_0^2}{1 + n J_0^2 \tau_0^2}. \tag{5}$$

The comparison of Eqs. (3) and (5) shows that under the approximation of sudden collisions for the considered model, the efficiency of the spin exchange of the pair of molecules in one collision is determined by the effective time: $\tau_{\mathrm{eff}} = (\sqrt{n})\tau_{\mathrm{c}}$,

$$P_{\mathrm{ex}} = \frac{1}{2} \frac{J_0^2 \tau_{\mathrm{eff}}^2}{1 + J_0^2 \tau_{\mathrm{eff}}^2}. \tag{6}$$

It should be noted that in the considered phenomenological model, the effective time determining the efficiency of the spin exchange is less than the sum of the times of residence of two spins in the exchange interaction region on average in one collision, $\tau_{\mathrm{eff}} = (\sqrt{n})\tau_{\mathrm{c}} < n\tau_{\mathrm{c}}$. In the general case, when in the interval between re-encounters of spins in the pair the quantum coherence between states $|1\rangle$ and $|2\rangle$ is destroyed only partially, the effective time of the spin exchange is supposed to be in the limits $(\sqrt{n})\tau_{\mathrm{c}} \leq \tau_{\mathrm{eff}} \leq n\tau_{\mathrm{c}}$.

For particles with spin ½ in the half of encounters the spins of colliding particles are oriented similarly, A↑ + B↑ = A↑ + B↑, and therefore no spin exchange occurs. With allowance for this, the average efficiency of the spin exchange in one encounter of A and B is the half of P_{ex}. We note that in EPR experiments in dilute solutions of paramagnetic particles, the EPR spectrum of separate spins, but not the spectrum of collided pairs, is measured. Therefore, the difference of the populations of the states of one spin with two different spin projections is observable. In the kinetic equations for density matrices of single spins, not $P_{\mathrm{ex}}/2$, but P_{ex}, serves as the efficiency of the spin exchange in one collision [see [2], Eq. (I.143)].

Within the model of the sudden switching of the exchange interaction at the collision radius, the rate constant of the spin exchange is:

$$K_{\mathrm{ex}} = P_{\mathrm{ex}} 4\pi r_0 D_{\mathrm{AB}}. \tag{7}$$

This rate constant can be written in the form of the Smoluchowski equation [see Eq. (1)], if the effective radius of the spin exchange $r_{\mathrm{eff}} = P_{\mathrm{ex}} r_0$ is introduced. Then Eq. (7) can be written in the form [cp. with Eq. (1)]:

$$K_{\mathrm{ex}} = 4\pi r_{\mathrm{eff}} D_{\mathrm{AB}}.$$

Equations (3–7) are widely used for calculating the rate constant of the spin exchange. Under the condition of sufficiently strong exchange interaction at the collision radius, when $J_0 \tau_{\mathrm{eff}} > 1$, the rate constant of the spin exchange (7) reaches its maximum value, which is the half of the rate constant of the first encounters [see Eq. (1)]:

$$K_{\mathrm{exmax}} = (1/2) 4\pi r_0 D_{\mathrm{AB}}. \tag{8}$$

This situation is called the case of the strong spin exchange.

Expressions (3–8) show that under the approximation of sudden switching of the exchange interaction only at the collision radius, the effective radius of the spin exchange is less than half of the collision radius $r_{\text{eff}} = r_0 P_{\text{ex}} \leq (1/2)\ r_0$. In real systems, the exchange interaction may cause spin exchange also at distances larger than the collision radius, and the spin exchange may occur not only in the moments of the closest approach of particles, but also at intervals between the re-encounters. As a result, the effective radius of the spin exchange can be larger than the collision radius. To take into account the extended character of the exchange interaction, it is necessary to know the dependence of the exchange integral on the distance between paramagnetic particles. It is expected that under good approximation, the exchange integral decreases with the increase in the distance r between paramagnetic particles according to the exponential law (see, e.g., [2])

$$J(r) = J_0 \exp\{-\text{æ}(r - r_0)\}. \tag{9}$$

Here, æ characterizes the slope of the decay of the exchange integral with the increase in the distance between spins A and B.

For neutral paramagnetic particles, the constant of the spin exchange rate with allowance for spatially extended character of the exchange interaction (9) and all re-encounters was calculated in [11, 12]. For particles with spin ½, the spin exchange effective radius is

$$r_{\text{eff}} = \frac{r_0}{2} + \text{Re}\left\{\frac{1}{\text{æ}}\left[\ln\left(\frac{z_0}{2}\right) + C - C_1'\right]\right\}, \tag{10}$$

$$z_0 = 2\sqrt{\frac{-iJ_0}{D_{AB}\text{æ}^2}}, C \approx 0.57721566\ldots \text{ Euler constant,}$$

$$C_1' = \frac{\pi}{2}\frac{N_1(z_0)z_0\text{æ}r_0 - 2N_0(z_0)}{J_1(z_0)z_0\text{æ}r_0 - 2J_0(z_0)}.$$

Here, J_k and N_k are the Bessel functions of the first and second kind.

To illustrate the behavior of the effective radius of the spin exchange with the increase in the exchange integral, Fig. 2 shows this dependence of r_{eff} for the model situation calculated using Eq. (10).

In Fig. 2, the abscissa for the exchange integral uses the log scale to present the variation of the exchange integral J_0 in the wide interval $\{10^8 \text{ rad/s}, 10^{16} \text{ rad/s}\}$. On the basis of Fig. 2, it is possible to state the following. With the increase in the exchange integral the effective radius of the spin exchange increases. In the region of the strong exchange interaction, when $|J_0|/(D_{AB}\ \text{æ}^2) > 1$,

$$r_{\text{eff}} \approx \frac{r_0}{2} + \frac{1}{2\text{æ}}\left[\ln\left(\frac{|J_0|}{D\text{æ}^2}\right) + 2C\right]. \tag{11}$$

We note that in the model of sudden collisions disregarding the extended character of the exchange interaction, the effective radius of the spin exchange [see Eqs. (5–7)] tends to the limiting value $r_0/2$ with the increase in the exchange integral value at the collision radius. Spin exchange with allowance for the extended exchange interaction is characterized by the effective radius of the spin exchange r_{eff} [Eq. (10)], which cannot be presented as a product of the collision radius r_0 and
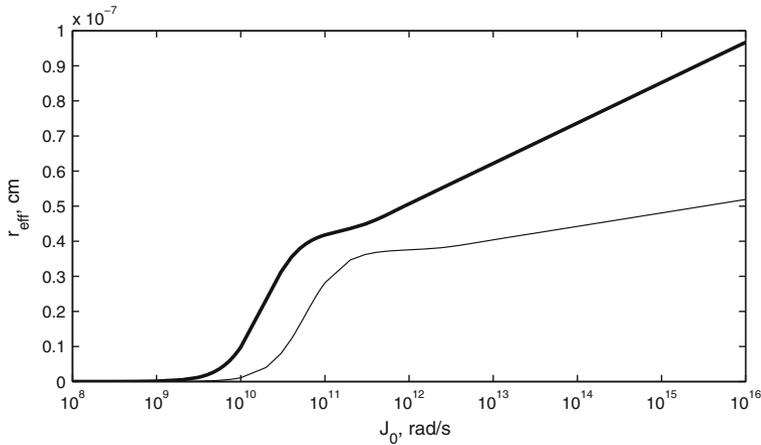
Fig. 2 Dependence of r_{eff} [Eq. (10)] on the exchange integral value J_0 at the collision radius calculated for two values of the slope æ of the exchange integral decay with the increase in the distance between two colliding paramagnetic particles: fast decay of the exchange integral, $æ = 3 \times 10^8$ cm^{-1} (*thin curve*), and relatively slow decay of the exchange integral $æ = 10^8$ cm^{-1} (*thick curve*). Calculations were performed for $r_0 = 7 \times 10^{-8}$ cm, $D_{AB} = 1.38 \times 10^{-5}$ cm^2/s. Note that in this case the limiting value of the effective radius expected in the framework of the sudden collisions model is 3.5×10^{-8} cm

the probability P_{ex} of the spin exchange in one collision, $r_{eff} \neq P_{ex}r_0$. To confirm this, it suffices to indicate that according to Eq. (10) and Fig. 2, r_{eff} can also be larger than r_0, while in the model of sudden collisions $P_{ex}r_0 \leq r_0/2$.

With a decrease in a value of æ, the volume of the region, in which the spin exchange can occur, increases. Figure 2 demonstrates the increase in the effective radius of the spin exchange with a decrease in the value of æ. With the increase in the diffusion coefficient of molecules, the effective time of collision of molecules decreases which should decrease the efficiency of the spin exchange. Equation (10) confirms the expected dependence of the effective radius of the spin exchange on the diffusion coefficient.

Thus, the theory of binary collisions between neutral molecules, including the theory of spin exchange, is developed rather well (see, e.g., [1, 2, 8, 9]) and applied successfully (see, e.g., [2, 13]).

The situation for charged particles is studied much less, and the theoretical analysis of the spin exchange during the collisions of charged paramagnetic particles is a topical problem (see, e.g., [2, 13]). The frequency of the first encounters for charged particles was calculated by Debye [14]. The rate constant of the first encounters is

$$K = f4\pi r_0 D_{AB},$$

$$f = \left\{ r_0 \int_{r_0}^{\infty} \exp\left(\frac{U(r)}{kT}\right) \frac{dr}{r^2} \right\}^{-1}, \tag{12}$$

where $U(r)$ is the potential energy of the electrostatic interaction of charged molecules A and B. The expression for f is given for the case when molecules A and

B are simulated by spheres with the same radii [15]. In the case of molecules of like charge, the Coulomb repulsion decreases the rate constant of binary collisions in comparison with the situation for neutral molecules, i.e., $f < 1$, while in the case of oppositely charged particles $f > 1$. The Coulomb interaction affects not only the rate constant of bimolecular collisions, but also the efficiency of the spin exchange, since it changes the average time of an encounter and the average time between re-encounters, average number of re-encounters and also the trajectory of the diffusion walk of a pair of molecules in the exchange interaction region.

If the electrostatic interaction has the form $U(r) = q_1 q_2/(\varepsilon r)$, where q_1 and q_2 are charges of two colliding particles and ε is the dielectric permittivity of the medium, then for particles of like charge the factor f [Eq. (12)] is

$$f_1 = \frac{R_{\text{On}}}{r_0} \frac{\exp(-R_{\text{On}}/r_0)}{1 - \exp(-R_{\text{On}}/r_0)}, \tag{13}$$

where $R_{\text{On}} = |q_1 q_2|/(\varepsilon k T)$ is the Onsager radius [15]. The Coulomb interaction energy at the Onsager radius is equal to the thermal energy kT. At room temperatures for single-charged particles for water ($\varepsilon \approx 81$), the Onsager radius $R_{\text{On}} \approx 7 \times 10^{-8}$ cm. For a solution with $\varepsilon \approx 10$ we have $R_{\text{On}} \approx 56 \times 10^{-8}$ cm. Thus, one can expect that in many cases the Onsager radius is much larger than the collision radius, i.e., $R_{\text{On}} > r_0$. In this situation,

$$f_1 \approx (R_{\text{On}}/r_0)\exp(-R_{\text{On}}/r_0). \tag{14}$$

The factor (14) reaches its maximum value $e^{-1} \approx 0.37$ at $R_{\text{On}}/r_0 = 1$. At $(R_{\text{On}}/r_0) > 3$ the factor $f_1 \ll 0.1$. The rate constant of the first encounters for particles of like charge (12) has the form:

$$K = 4\pi D_{\text{AB}} R_{\text{On}}\exp(-R_{\text{On}}/r_0). \tag{15}$$

The effective collision radius of particles of like charge is given by Eq. (16) and according to the above estimates this radius is expected to be typically less than the collision radius r_0,

$$r_{\text{eff}} = R_{\text{On}}\exp(-R_{\text{On}}/r_0) < r_0. \tag{16}$$

For oppositely charged particles, the factor f [Eq. (12)] has the form:

$$f_2 = \frac{R_{\text{On}}/r_0}{1 - \exp(-R_{\text{On}}/r_0)}. \tag{17}$$

According to the above estimates, the factor f_2 in good approximation can be considered as:

$$f_2 \approx R_{\text{On}}/r_0. \tag{18}$$

In this situation, the rate constant of the first encounters of oppositely charged particles (12) has the form:

$$K = 4\pi D_{\text{AB}} R_{\text{On}}, \tag{19}$$

and the effective meeting radius of oppositely charged particles is close to the Onsager radius

$$r_{\text{eff}} = R_{\text{On}} > r_0. \tag{20}$$

This is an expected result. In fact, oppositely charged particles reach the collision radius, if they approach the Onsager radius.

At present, in the analysis of the experimental data on spin exchange between charged paramagnetic particles in dilute solutions, it is conventionally assumed that the rate constant can be described using Eq. (12) with the additional factor P_{ex}, which describes the efficiency of the spin exchange during a collision [2, 16]:

$$K_{\text{ex}} = P_{\text{ex}} f 4\pi r_0 D_{\text{AB}}. \tag{21}$$

In the approximation of the sudden switching of the exchange interaction, P_{ex} is given by Eq. (6). Within this approach, determining K_{ex} from the EPR experiments and calculating P_{ex}, it is possible to find the rate of binary collisions of charged particles. It is necessary to take into account that the Coulomb interaction between colliding partners affects the average time of an encounter at the collision radius. In comparison with the analogous neutral molecules, the collision time τ_{eff} for particles of like charge should be less than for neutral particles, but for oppositely charged particles it should be larger.

The effective encounter time τ_{eff} can be estimated as follows. In the thermodynamic equilibrium, the flow of pairs of particles into the interaction region $Z_+ = f 4\pi r_0 D_{\text{AB}} C_{\text{B}}$ should be equal to the flow of pairs from the collision region $Z_- = v \exp(-U(r_0)/kT) C_{\text{B}}/t_{\text{eff}}$. Here, $v = 4\pi r_0^2 \delta$, $v \exp(-U(r_0)/kT) C_{\text{B}}$ is the number of pairs in the region of the exchange interaction. From the condition of the equality of these flows, $Z_+ = Z_-$ (the condition of detailed balance), we find the effective collision time of the charged particles in the region between two spheres with radii r_0 and $r_0 + \delta$

$$\tau_{\text{eff}} = \frac{r_0 \delta}{f D_{\text{AB}}} \exp\left(-\frac{U(r_0)}{kT}\right). \tag{22}$$

If the electrostatic interaction has the form $U(r) = q_1 q_2/(\varepsilon r)$, the effective encounter time of charged particles in the interaction region can be estimated using the values of factor f presented, e.g., in Eqs. (14, 18). For particles of like charge, using Eqs. (14, 22) we obtain:

$$\tau_{\text{eff}} = \frac{r_0 \delta}{D_{\text{AB}}} \frac{r_0}{R_{\text{On}}} < \frac{r_0 \delta}{D_{\text{AB}}}. \tag{23}$$

For oppositely charged particles, using Eqs. (18, 22), we obtain

$$\tau_{\text{eff}} = \frac{r_0 \delta}{D_{\text{AB}}} \frac{r_0}{R_{\text{On}}} \exp\left(\frac{R_{\text{On}}}{r_0}\right) > \frac{r_0 \delta}{D_{\text{AB}}}. \tag{24}$$

In fact, the exchange interaction not only acts at the approach to the collision radius, but spin exchange can also occur at larger distances between particles. This can be of especially high importance for particles of like charge. In this case the Coulomb repulsion hampers the maximum approach of spins and therefore the spin exchange at large distances between particles becomes important. This means that the model of the sudden switching of the exchange interaction might be a poor basis

for the analysis of spin exchange between charged paramagnetic particles. In Sect. 2.4, we will consider this issue.

1.2 The Aim of This Work

In the brief review presented, it was shown that there exists a rather well-developed theoretical description of the bimolecular spin exchange in dilute solutions of the neutral paramagnetic particles. There are analytical solutions for model situations which are used successfully when interpreting experimental data.

However, the theory is much less developed in the case of the bimolecular spin exchange between charged paramagnetic particles. In this case, new important physical parameters appear which characterize the electrostatic interaction and affect the bimolecular spin exchange rate: the Debye screening radius, Onsager radius and the dielectric permittivity of the medium.

In the case of charged as well as neutral particles, the constant of the spin exchange rate can be expressed in terms of the effective exchange radius:

$$K_{\text{ex}} = 4\pi r_{\text{eff}} D_{\text{AB}}. \tag{25}$$

The effective radius r_{eff} combines the effects from the parameters of the exchange interaction, Coulomb interaction between particles and molecular-kinetic parameters of the mutual diffusion motion of particles.

According to the existing theoretical ideas, the calculation of the effective radius of the bimolecular processes is reduced to solving equations for the operator of the efficiency of a collision [1, 2, 11, 12, 17, 18]. The aim of this work is to develop the theory of spin exchange between charged paramagnetic particles.

In Sect. 2, we present the kinetic equations for the spin density matrices of paramagnetic particles taking into account their binary collisions. These kinetic equations provide the equations for the operator of the efficiency of the spin exchange during the collision of charged particles. The equations obtained cannot be solved analytically. Therefore, the effective radius of the spin exchange and the constants of the spin exchange rate were calculated numerically. The effective radius of the spin exchange is analyzed as a function of the molecular diffusion coefficient, the electrostatic interaction parameters of the electrolyte and exchange interaction parameters. To illustrate the potential of the theory developed in this work, we have used data taken from the literature [16]. It is demonstrated that the developed theory provides a basis for the analysis of experiment.

2 Theory of Bimolecular Spin Exchange Between Charged Paramagnetic Particles

2.1 Mathematical Apparatus

Let us consider the dilute solution of charged particles with spins ½. Let us assume that the concentration of spins is sufficiently low to limit ourselves to taking into account collisions of two spins and ignore the probability of the simultaneous

collisions of three and more spins. This assumption is justified, if the concentration of spins C satisfies the condition $(4\pi/3)r_{\text{eff}}^3 C \ll 1$.

If concentration C is measured in M/L units, this condition is reduced to $C \ll 1$ M. When this condition is fulfilled, the set of all spins can be divided into an ensemble of separate particles and another of pairs of particles with the interaction inside the pairs. Free particles when approaching may form pairs or pairs decay, i.e., spins move from one ensemble into another. The relative motion of partners in the pair randomly modulates the interaction between spins. In addition, the Coulomb interaction between charged particles repulses like charges and attracts opposite charges that affects the probability of their approach to the distance of the effective spin–spin interaction. The theory is developed within the assumption that the change of the spins states of interacting particles does not affect their diffusion motion. Under this assumption, we consider the distance r between partners in the pair as the external classical parameter for the quantum–mechanical problem about the spin evolution of an ensemble of pairs. The relative motion of partners in the pair is described using the model of continuous diffusion.

In [1, 2, 5, 11, 12, 17, 18], a formalism was proposed, using which the kinetic equations were derived for one-particle spin density matrices σ_A and σ_B of the subsystems A and B with allowance for binary collisions:

$$\begin{aligned}
\frac{d\hat{\sigma}_A(t)}{dt} &= -\frac{i}{\hbar}\left[\hat{H}_A, \hat{\sigma}_A\right] - C_A Tr_2\left[\hat{\hat{P}}_{AA}\hat{\sigma}_A \otimes \hat{\sigma}_A\right] - C_B Tr_B\left[\hat{\hat{P}}_{AB}\hat{\sigma}_A \otimes \hat{\sigma}_B\right], \\
\frac{d\hat{\sigma}_B(t)}{dt} &= -\frac{i}{\hbar}\left[\hat{H}_B, \hat{\sigma}_B\right] - C_B Tr_2\left[\hat{\hat{P}}_{BB}\hat{\sigma}_B \otimes \hat{\sigma}_B\right] - C_A Tr_A\left[\hat{\hat{P}}_{AB}\hat{\sigma}_A \otimes \hat{\sigma}_B\right].
\end{aligned} \tag{26}$$

In these equations, P_{AA}, P_{BB} and P_{AB} denote operators of collisions (more exactly, superoperators) determining the efficiency of the spin exchange in collisions of particles in different possible combinations AA, AB and BB in the pair. Let us consider the process of collisions of particles of different kinds, A + B. Equations for the operator P_{AB} are derived from the following considerations.

Let us consider a pair of colliding particles A and B. Its spin Hamiltonian in the external constant magnetic field H has the form:

$$\begin{aligned}
\hat{H}(\vec{r}) &= \hat{H}(r) = \hat{H}_0 + \hbar J(r)\hat{S}_A\hat{S}_B, \\
\hat{H}_0 &= \hat{H}_A + \hat{H}_B, \ J(r) = J_0\exp\{-\text{æ}(r - r_0)\}, \\
\hat{H}_A &= g_A\beta H\hat{S}_{AZ} = \hbar\omega_A\hat{S}_{AZ}, \ \hat{H}_B = g_B\beta H\hat{S}_{BZ} = \hbar\omega_B\hat{S}_{BZ}.
\end{aligned} \tag{27}$$

Let us divide the ensemble of all pairs into subensembles with a given distance r between partners in the pair A and B. The kinetic equation for the partial density matrix of the isolated pair of the pairs with a given r, $\rho(r, t)$, has the form

$$\frac{\partial\hat{\rho}(\vec{r}, t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}(r), \hat{\rho}(\vec{r}, t)] + \hat{L}(\vec{r})\hat{\rho}(\vec{r}, t). \tag{28}$$

The last term in (28) is the divergence of the flow of the partial density matrix. The summary flow j into the subensemble with the given r consists of two components: the equilibration of the concentrations according to the Fick law and the motion under the action of the forces of the Coulomb interaction:

$$\vec{j} = -D_{AB}\nabla\rho(\vec{r},t) + \rho(\vec{r},t)\vec{v}(\vec{r}),$$

$$\vec{v}(\vec{r}) = \mu\vec{F}(\vec{r}) = -\frac{D_{AB}}{kT}\nabla U(\vec{r}), \quad U(\vec{r}) = U(r) = \frac{q_A q_B}{\varepsilon r}e^{-r/r_D}, \tag{29}$$

where q_A and q_B are charges of partners in the pair, r_D is the Debye screening radius, D_{AB} is the coefficient of mutual diffusion of A and B, k is the Boltzmann constant, T is the temperature and ε is the dielectric permittivity of a solution.

Within the model of continuous diffusion we have:

$$\hat{L}(\vec{r}) = \hat{L}(r) = D_{AB}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{D_{AB}q_A q_B}{\varepsilon kTr^2}\left(\left(1 + \frac{r}{r_D}\right)\frac{\partial}{\partial r} - \frac{r}{r_D^2}\right)e^{-r/r_D}. \tag{30}$$

It is well known from statistical mechanics that the change of the one-particle spin density matrix can be expressed in terms of the pair density matrix. In the considered problem for the one-particle density matrix, e.g., particles A, with allowance for the pair interaction only with particles B, $V_{AB}(\boldsymbol{r})$, we have the following equation [19]:

$$\frac{d\hat{\sigma}_A(t)}{dt} = -\frac{i}{\hbar}\left[\hat{H}_A, \hat{\sigma}_A(t)\right] - \frac{1}{V}Tr_B\sum_{K=1}^{N_B}\int\frac{i}{\hbar}\left[\hat{V}_{AB}(\vec{r}_K), \hat{\rho}_2(\vec{r}_K,t)\right]d\vec{r}_K. \tag{31}$$

Integration is performed over all possible positions of the κ-th particle B with respect to the particle A, summation is performed over all particles B, and Tr_B means convolution over spins states of particles B. In the thermodynamic limit when $V, N_B \to \infty$ so that $N_B/V \to C_B$, with allowance for the fact that all particles B on average give the same contribution in collisions with particles A, we have

$$\frac{d\hat{\sigma}_A(t)}{dt} = -\frac{i}{\hbar}\left[\hat{H}_A, \hat{\sigma}_A(t)\right] - C_B Tr_B\int\frac{i}{\hbar}\left[\hat{V}_{AB}(\vec{r}), \hat{\rho}_2(\vec{r},t)\right]d\vec{r}. \tag{32}$$

In the general case the change of the two-particle density matrix is "caught on" the three-particle density matrix. But in the binary collisions approximation, we ignore the contribution of triple collisions. Therefore in (32), one can use the density matrix $\rho(r, t)$ as a two-particle density matrix $\rho_2(r, t)$ found from the solution of Eq. (28). To obtain the kinetic Eq. (26), the pair density matrix in Eq. (32) is expressed in terms of one-particle matrices, and to this end the solution of Eq. 28) is sought for in the Liouville representation in the form (see [1, 19])

$$\hat{\rho}(r,t) \approx \hat{\hat{G}}(r,t)\hat{\sigma}_A(t) \otimes \hat{\sigma}_B(t). \tag{33}$$

The direct product $\sigma_A(t) \times \sigma_B(t)$ is the matrix 4×4. We consider it as a 16-vector elongated into the line over columns, and (33) as the action of a certain linear correlator "superoperator" $G(r, t)$ (matrices 16×16) on this vector. Substituting (33) into (28) and taking into account that in (28) the interaction of a selected pair is taken into account explicitly, we finally obtain the equation for G.

Using Eq. (33), the left-hand side of Eq. (28) is presented in the form:

$$\frac{d\hat{\rho}(r,t)}{dt} = \frac{d\hat{\hat{G}}(r,t)}{dt}\hat{\sigma}_A \otimes \hat{\sigma}_B + \hat{\hat{G}}(r,t)\frac{d\hat{\sigma}_A}{dt} \otimes \hat{\sigma}_B + \hat{\hat{G}}(r,t)\hat{\sigma}_A \otimes \frac{d\hat{\sigma}_B}{dt}.$$

According to the arguments presented above, in the time scale of the "lifetime" τ_p of the pairs we use the approximation:

$$\frac{d\hat{\sigma}_A(t)}{dt} = -\frac{i}{\hbar}\left[\hat{H}_A, \hat{\sigma}_A(t)\right], \frac{d\hat{\sigma}_B(t)}{dt} = -\frac{i}{\hbar}\left[\hat{H}_B, \hat{\sigma}_B(t)\right].$$

This approximation means that in the time scale of a collision of two molecules, we ignore the change of the one-particle density matrix due to binary collisions, since the binary collisions change the one-particle matrix at the times of the "mean free path" between binary collisions.

From (28), we obtain equation for the correlator $G(r, t)$

$$\frac{\partial\hat{\hat{G}}(r,t)}{\partial t} = \hat{\hat{L}}\hat{\hat{G}}(r,t) + \hat{\hat{W}}(r)\hat{\hat{G}}(r,t) + [\hat{\hat{Q}}_0, \hat{\hat{G}}(r,t)], \tag{34}$$

where $\hat{\hat{W}}(r) = iJ(r)\left[\left(\hat{S}_A\hat{S}_B\right)^{tr}\otimes\hat{1}_4 - \hat{1}_4 \otimes \left(\hat{S}_A\hat{S}_B\right)\right],\ \hat{\hat{Q}}_0 = \frac{i}{\hbar}\left[\hat{H}_0^{tr} \otimes \hat{1}_4 - \hat{1}_4 \otimes \hat{H}_0\right].$ Here H^{tr} means transposed operator.

Here, all operators (with one hat) are given in the Gilbert space of the pair of spins and $\hat{1}_4$ is the unity operator there. In the stationary regime, at times $t \gg \tau_p$, $G(r,t)$ satisfies stationary equation

$$\hat{\hat{L}}(r)\hat{\hat{G}}(r) + \hat{\hat{W}}(r)\hat{\hat{G}}(r) + [\hat{\hat{Q}}_0, \hat{\hat{G}}(r)] = 0. \tag{35}$$

Let us formulate the boundary conditions for the correlator $G(r)$. When the partners in the pair move apart, the correlation between their spin states should weaken [19]. From this we have the first boundary condition:

$$\lim_{r \to \infty} \hat{\hat{G}}(r) = \hat{\hat{1}}_{16}. \tag{36}$$

Assuming that at the radius of the closest approach the total flow of pairs of spins is zero, we have second boundary condition $j(r = r_0) = 0$, or

$$\frac{\partial\hat{\hat{G}}(r_0)}{\partial r} = \frac{q_A q_B}{\varepsilon k T r_0^2}\left(1 + \frac{r_0}{r_D}\right)e^{-\frac{r_0}{r_D}}\hat{\hat{G}}(r_0). \tag{37}$$

The superoperator $\hat{\hat{P}}$ (impact operator) describes the change of the pair density matrix in the interaction region and, according to Eqs. (32, 33), is determined by the expression:

$$\hat{\hat{P}}_{AB} = \int \hat{\hat{W}}(r)\hat{\hat{G}}(r)d\vec{r}. \tag{38}$$

Substituting Eqs. (33), (34), (38) into (32) and repeating all these expressions for the cases of collisions of particles of the same kind, we come to the kinetic equations for spin density matrices [Eq. (26)].

The coefficients of kinetic equations give the rate constants of the binary process of the spin exchange. With these coefficients, one can determine the effective radius of the spin exchange (21).

Thus, these relations are the mathematical apparatus for calculating the efficiency of binary collisions. In the situation considered, the kinetic equations cannot be solved analytically, and it is necessary to perform numerical calculations. The algorithm of the numerical calculations is given below.

2.2 Algorithm of the Numerical Calculation of the Effective Radius of Spin Exchange

The substitution $x = r/r_D$ transforms the boundary value problem (32) and the boundary conditions (33) and (34) into the dimensionless form:

$$\hat{\hat{G}}''_{xx} + \frac{2}{x}\hat{\hat{G}}'_x - \zeta\left(\left(1 + \frac{1}{x}\right)\hat{\hat{G}}'_x - \hat{\hat{G}}\right)\frac{e^{-x}}{x} + \hat{w}_0 e^{-\tilde{æ}x}\hat{\hat{G}} + [\hat{\hat{q}}_0, \hat{\hat{G}}] = 0, \qquad (39)$$

$$\hat{w}_0 = \frac{r_D^2}{D}\hat{W}(r_0), \ \hat{\hat{q}}_0 = \frac{r_D^2}{D}\hat{\hat{Q}}_0, \ \zeta = \frac{q_A q_B}{\varepsilon r_D kT}, \ \tilde{æ} = æ r_D,$$

$$\lim_{x \to \infty}\hat{\hat{G}}(x) = \hat{\hat{1}}_{16}, \ \frac{\partial \hat{\hat{G}}(x_0)}{\partial x} = \zeta\left(\frac{1 + x_0}{x_0^2}\right)e^{-x_0}\hat{\hat{G}}(x_0), \ x_0 = r_0/r_D.$$

The problem (39), in turn, is transferred to finite interval [0,1] by the fractional-linear transformation $y = 1 - x_0/x$ and takes the form:

$$\frac{(1-y)^4}{x_0^2}\hat{\hat{G}}''_{yy} - \zeta\left[\left[\frac{(1-y)^3}{x_0^2} + \frac{(1-y)^2}{x_0}\right]\hat{\hat{G}}'_y - \hat{\hat{G}}\right]\frac{1-y}{x_0}e^{-\frac{x_0}{1-y}} + \hat{w}_0 e^{-\frac{æ r_0}{1-y}}\hat{\hat{G}} + [\hat{\hat{q}}_0, \hat{\hat{G}}] = 0,$$

$$(40)$$

$$\lim_{y \to 1}\hat{\hat{G}}(y) = \hat{\hat{1}}_{16}, \ \frac{\partial \hat{\hat{G}}(0)}{\partial y} = \zeta\left(1 + \frac{r_D}{r_0}\right)e^{-\frac{r_0}{r_D}}\hat{\hat{G}}(0),$$

suitable for the numerical solution by the finite-differential method.

The impact operator at this substitution has the form:

$$\hat{\hat{P}}_{AB} = 4\pi D_{AB}\frac{r_0^3}{r_D^2}\hat{w}_0\int_0^1 \frac{\hat{\hat{G}}(y)}{(1-y)^4}e^{-\frac{æ r_0}{(1-y)}}dy. \qquad (41)$$

Equation (33) contains a commutator $[\hat{\hat{q}}_0, \hat{\hat{G}}]$ that makes it inconvenient for the standard matrix calculations. Therefore in (40), let us use again the Liouville representation. Let us denote as $\widetilde{G}$ the vector with the dimensionality 256×1 obtained by the elongation of the matrix $\hat{\hat{G}}$ over the columns in a line, and denote vectors obtained in the same manner from matrices $\hat{\hat{1}}_{16}$ and $\hat{\hat{0}}_{16}$ as $\tilde{1}_{16}$ and $\tilde{0}_{16}$.

Let us introduce $\tilde{l}, \tilde{k}, \tilde{m}$, and then $\tilde{u}$ and $\tilde{v}$ according to formulas

$$\tilde{l}(y) \stackrel{\text{def}}{=} \frac{(1-y)^4}{x_0^2} \hat{\tilde{1}}_{16} \otimes \hat{\tilde{1}}_{16}, \quad \tilde{k}(y) \stackrel{\text{def}}{=} -\zeta \left[\frac{(1-y)^4}{x_0^3} + \frac{(1-y)^3}{x_0^2} \right] e^{-\frac{x_0}{1-y}} \hat{\tilde{1}}_{16} \otimes \hat{\tilde{1}}_{16},$$

$$\tilde{m}(y) \stackrel{\text{def}}{=} \zeta \frac{1-y}{x_0} e^{-\frac{x_0}{1-y}} \hat{\tilde{1}}_{16} \otimes \hat{\tilde{1}}_{16} + \hat{\tilde{1}}_{16} \otimes \hat{\tilde{w}}_0 e^{-\frac{\text{æ}x_0}{1-y}} + \hat{\tilde{1}}_{16} \otimes \hat{\tilde{q}}_0 - \hat{\tilde{q}}_0^{\text{tr}} \otimes \hat{\tilde{1}}_{16},$$

$$\tilde{u}(y) = \tilde{k}(y)/\tilde{l}(y), \quad \tilde{v}(y) = \tilde{m}(y)/\tilde{l}(y). \tag{42}$$

Equation (40) with allowance for (42) takes the final form:

$$\tilde{G}_{yy}'' + \tilde{u}\tilde{G}_y' + \tilde{v}\tilde{G} = \tilde{0}_{16},$$

$$\tilde{G}(1) = \tilde{1}_{16}, \quad \tilde{G}_y'(0) = \zeta(1 + r_D/r_0)e^{-r_0/r_D}\tilde{G}(0), \tag{43}$$

where matrices $\tilde{u}$ and $\tilde{v}$ have the dimensionality 256×256.

Let us write the difference scheme for (42) with $N + 1$ sites equidistant over h:

$$\tilde{G}_{k-1} + (\tilde{v}_k h^2 - \tilde{u}_k h - 2\hat{\tilde{1}}_{16} \otimes \hat{\tilde{1}}_{16})\tilde{G}_k + (\hat{\tilde{1}}_{16} \otimes \hat{\tilde{1}}_{16} + h\tilde{u}_k)\tilde{G}_{k+1} = 0, \quad k = \overline{1, N-1},$$

$$\tilde{G}_0 = \tilde{G}_1 / \left[1 + h\zeta(1 + r_D/r_0)e^{-r_0/r_D} \right], \qquad \tilde{G}_N = \tilde{1}_{16}. \tag{44}$$

When solving the problem numerically, it appeared to be useful to perform the additional transformation [18], namely, to transform Eq. (40) to the Q_0 operator eigen basis. Due to this procedure, all superoperators in Eq. (44) become of the decomposable (step-matrices) form. As a result, the solution of the problem (44) is reduced to the finding of the 16 vectors of the 16-th dimension instead of finding one 256-th dimension vector.

As a result, the implementation of the scheme (44) demonstrated good convergence. The obtained solution was substituted into the formula for the impact operator (41), and the integral in it was calculated according to the Simpson formula.

2.3 Results of the Calculation of the Effective Radius of Spin Exchange for Charged Paramagnetic Particles with Spin ½

Using the above equations, r_{eff} for charged particles with spin ½ for different values of $J(r_0)$ and æ Eq. (9) was found.

Figure 3 illustrates the dependence of r_{eff} radius on $J(r_0)$. The analysis of curves given in Fig. 3a–c shows that the effective radius of the spin exchange increases with a decrease in the coefficient of the mutual diffusion of paramagnetic particles. This is explained by the fact that with a decrease in the mobility of molecules a time of the stay of two colliding particles in the region of the exchange interaction increases. The effective radius of the spin exchange for oppositely charged particles is larger than that for neutral particles, and the effective radius of the spin exchange for particles of like charge is less than that for neutral particles (see Fig. 3). This is an expected result qualitatively. But now we can calculate quantitatively the effect of the Coulomb interaction of charged particles on the spin exchange radius. In the case of neutral particles the effective radius of the spin exchange r_{eff} reduces to the linear dependence on ln|J$_0$| with an increase in the exchange integral J$_0$ on the
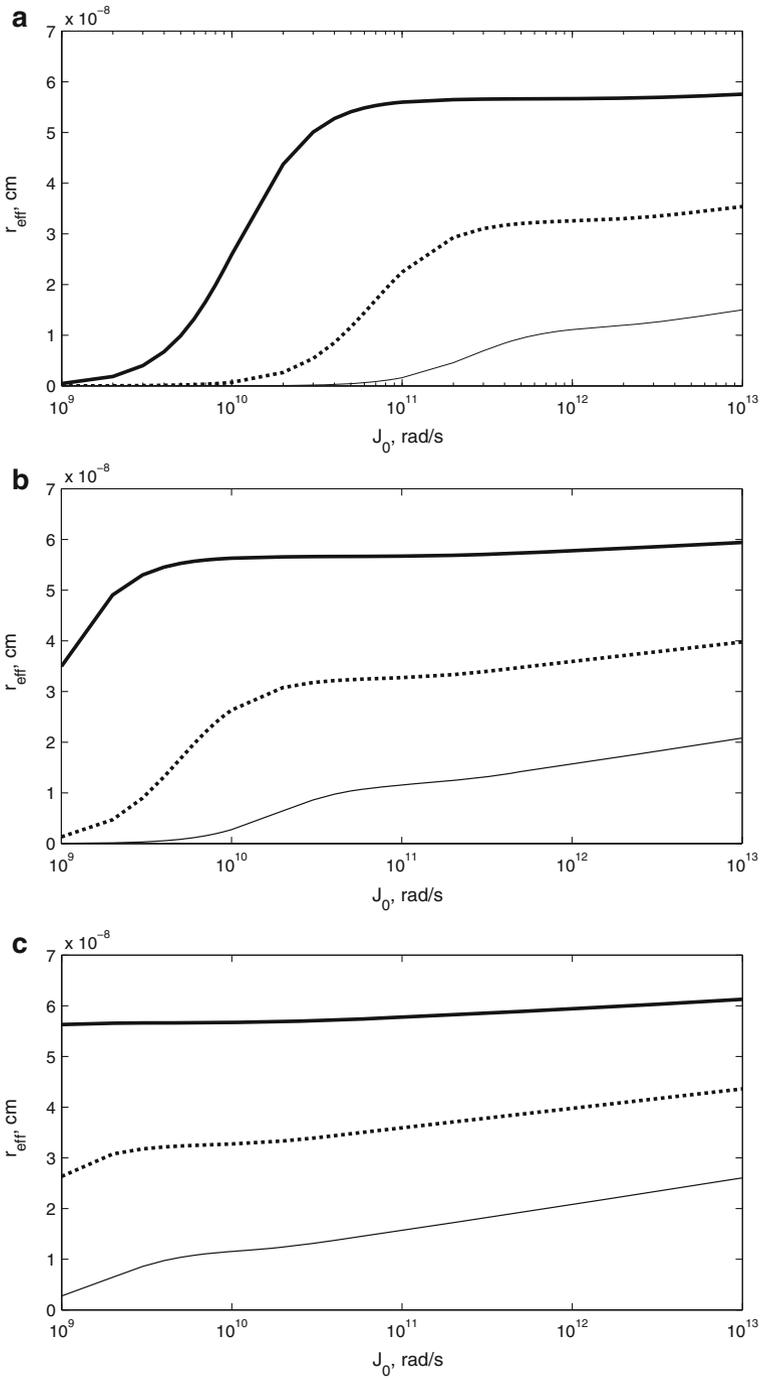
Fig. 3 Dependence of the effective radius of spin exchange on the exchange integral at the collision radius for different values of the diffusion coefficient of paramagnetic particles in a case of like charge (*thin solid curves*), for neutral particles (*thick dotted curve*) and for oppositely charged particles (*thick solid curve*). Calculations were performed for the following parameter values: $r_0 = 6 \times 10^{-8}$ cm, $æ = 3 \times 10^8$ cm^{-1}, $\varepsilon = 20$, $r_D = 10 \times 10^{-8}$ cm, **a** $D_{AB} = 1.38 \times 10^{-5}$ cm^2/s, **b** $D_{AB} = 10^{-6}$ cm^2/s, **c** $D_{AB} = 10^{-7}$ cm^2/s. Abscissa for the exchange integral J_0 uses the log scale to present the variation of the effective radius of spin exchange in the wide interval $\{10^9$ rad/s, 10^{13} rad/s$\}$

collision radius (see Eq. (11)). The numerical calculations also showed that for charged particles the effective radius of the spin exchange r_{eff} reduces to the linear dependence on $\ln|J_0|$ in the region of strong exchange (see Fig. 3). If the effective radius of the spin exchange is larger than one-half of the closest approach radius, the situation of the strong spin exchange takes place [cf. Eq. (9)]. Let us assume that the situation of the strong spin exchange is implemented, when the action of the exchange interaction, i.e., the product of the exchange integral $J(r_{eff})$ by the time τ_{eff} of residence of the particles in the interaction region is on the order of 1 (Note that the exchange integral is given in the units of rad/s). From this condition, $J_0 \exp(-ær_{eff})\tau_{eff} \approx 1$, we obtain the estimate of the effective radius of the strong spin exchange $r_{eff} \approx (1/æ) \ln(J_0\tau_{eff})$. In fact, τ_{eff} in turn can depend on r_{eff}, but this dependence is not exponential, it could be, e.g., quadratic $\tau_{eff} \approx r_{eff}^2/D_{AB}$ or linear $\tau_{eff} \approx r_{eff}/æD_{AB}$ or independent $\tau_{eff} \approx /æ^2D_{AB}$.

The effective time of the stay of particles in the region of the effective exchange interaction depends on æ. The faster the decay of the exchange integral, the less is the region of the effective interaction and, as a result, the less is the effective radius of spin exchange. This qualitative expectation is completely confirmed by the numerical calculations (see Fig. 4).

In the case of the spin exchange between charged particles, the Debye screening radius is an important parameter. With a decrease in the Debye screening radius, the role of the Coulomb interaction should decrease and the effective radius of the spin exchange should tend to the radius of the spin exchange for neutral particles. We performed numerical calculations, which completely confirmed these qualitative statements. Figure 5a, b illustrates that at $r_D = 1.6 \times 10^{-8}$ cm (when the Debye screening radius is much less than the collision radius), the effective radius of the spin exchange between charged particles almost coincides with the radius of the spin exchange for neutral particles. In the other example (see Fig. 5c, d), when $r_D = 10^{-7}$ cm is nearly two times larger than the collision radius $r_0 = 6 \times 10^{-8}$ cm, which we selected for these calculations, the Coulomb interaction quite strongly affects the radius of the spin exchange in comparison with the case of neutral particles. Curves (a, c) correspond to $æ = 10^8$ cm^{-1}; curves (b, d) correspond to $æ = 3 \times 10^8$ cm^{-1}.

The numerical calculations above show that at rather high values of the coefficient of mutual diffusion of particles and rather large slope of the exchange integral decay, the spin exchange is no longer strong even for collisions of oppositely charged particles, which can be kept in the interaction region by the Coulomb attraction for a relatively long time.
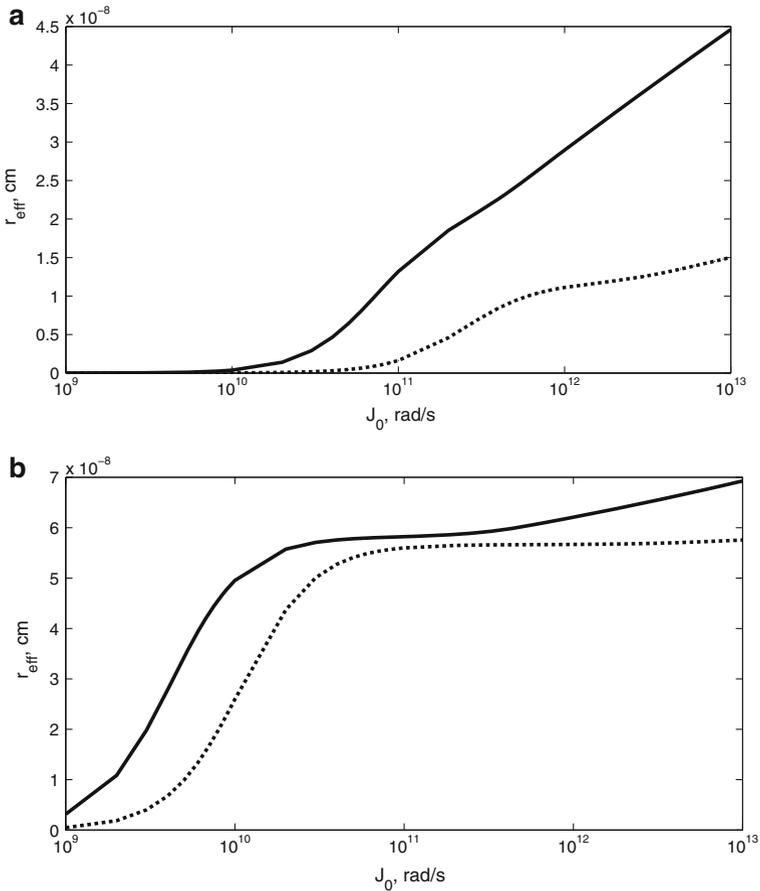
Fig. 4 Dependence on $J(r_0)$ of the effective radius of spin exchange between paramagnetic particles of like charged (**a**) and oppositely charged paramagnetic particles (**b**) for two values of the slope of the exchange integral decay with the increase in the distance between colliding paramagnetic particles: $\mathrm{æ} = 10^8$ cm^{-1} (*solid curves*), $\mathrm{æ} = 3 \times 10^8$ cm^{-1} (*dotted curves*). Calculations were performed for the following parameter values: $r_0 = 6 \times 10^{-8}$ cm, $\varepsilon = 20$, $r_D = 10 \times 10^{-8}$ cm, $D_{AB} = 1.38 \times 10^{-5}$ cm^2/s

Tables 1 and 2 summarize the calculated values of the effective radius of spin exchange for charged paramagnetic particles for a series of selected values of parameters, which affect the value of this radius.

Data given in these tables may be useful as references during the interpretation of experimental data. Data presented in these tables and Figs. 3, 4, 5 give an idea about the scale of the possible variations of the effective radius of the spin exchange during the variation of the molecular-kinetic parameters, and also parameters which characterize the exchange and electrostatic interaction between charged paramagnetic particles.
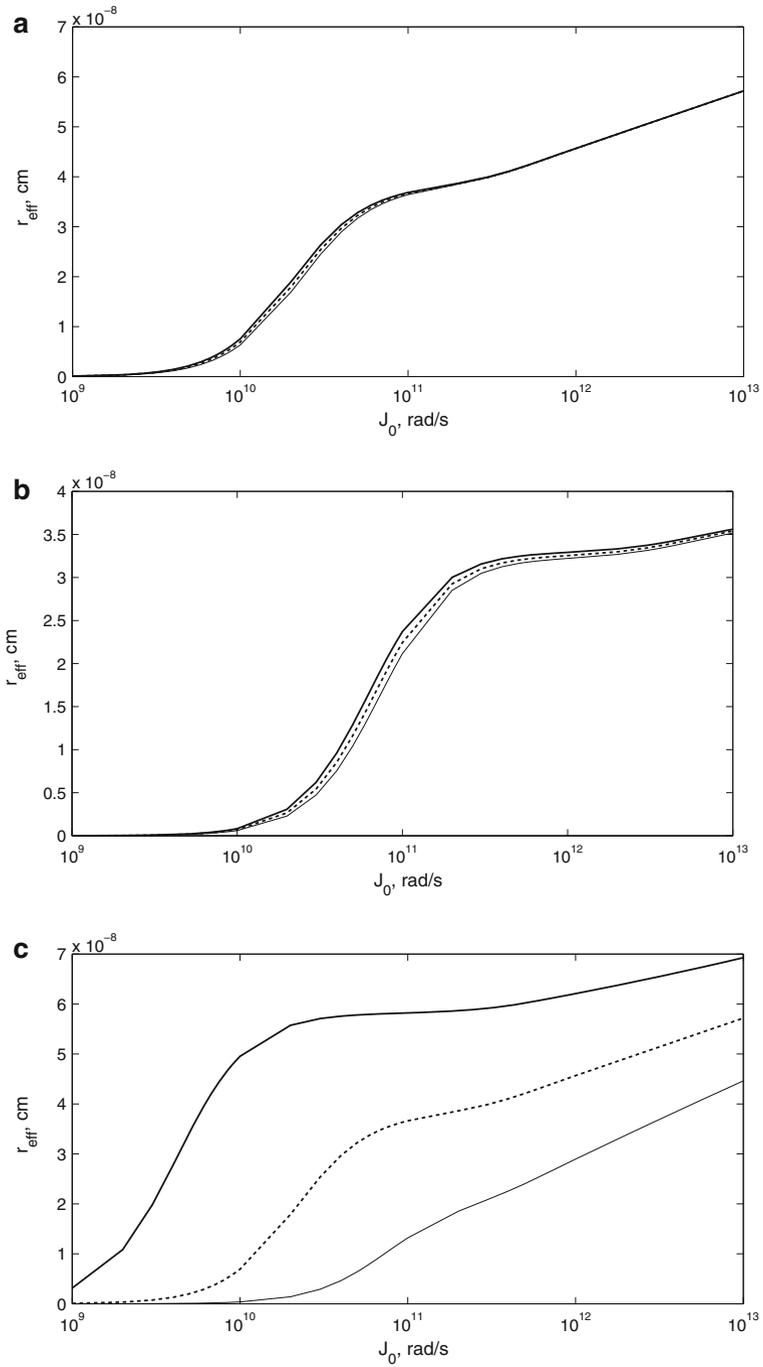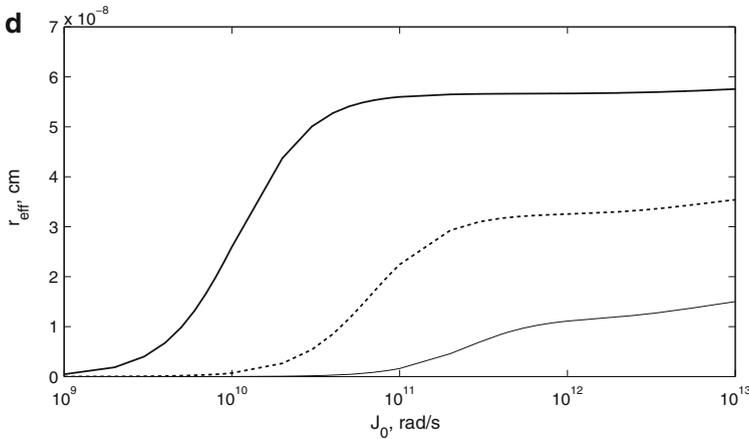
Fig. 5

Fig. 5 Comparison of effective radii of spin exchange for charged and neutral particles at different values of the Debye screening radius: **a**, **b** $r_D = 1.6 \times 10^{-8}$ cm, **c**, **d** $r_D = 10 \times 10^{-8}$ cm. Other calculation parameters are: $r_0 = 6 \times 10^{-8}$ cm, $\varepsilon = 20$, $D_{AB} = 10^{-5}$ cm^2/s. Abscissa for the exchange integral uses the log scale to present the variation of the effective radius of spin exchange in the wide interval $\{10^9$ rad/s, 10^{13} rad/s$\}$. *Thin solid curves* present the data for particles of like charge, *thick dotted curves* present data for neutral particles and *thick solid curves* are data for oppositely charged particles

Table 1 Values of the effective radius (in 10^{-8} cm units) of spin exchange between oppositely charged particles for a selected set of parameters of exchange and electrostatic interaction, and diffusion coefficient

J_0, rad/s	10^{10}				10^{11}				10^{12}				10^{13}			
æ, cm^{-1}	10^8		3×10^8		10^8		3×10^8		10^8		3×10^8		10^8		3×10^8	
D, cm^2/s	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}
$\varepsilon = 20$																
$r_D = 2A$	1.34	3.81	0.18	2.86	3.81	4.74	2.86	3.36	4.74	5.88	3.36	3.65	5.88	7.03	3.65	4.02
$r_D = 10A$	5.33	5.84	3.5	5.63	5.84	6.30	5.63	5.67	6.30	7.04	5.67	5.78	7.04	7.89	5.78	5.94
$\varepsilon = 81$																
$r_D = 2A$	1.88	3.78	0.14	2.69	3.78	4.73	2.69	3.3	4.73	5.88	3.3	3.61	5.88	7.03	3.61	3.99
$r_D = 10A$	2.01	4.30	0.34	3.51	4.30	5.13	3.51	3.89	5.13	6.17	3.89	4.15	6.17	7.25	4.15	4.48

The distance of the closest approach $r_0 = 6 \times 10^{-8}$ cm

2.4 Approximate Estimates of the Effective Radius of the Spin Exchange Between Charged Particles

In this work we developed a theory that makes it possible to calculate the effective radius of spin exchange between charged paramagnetic particles. The knowledge of this radius makes it possible also to calculate the rate constant of the spin exchange [see Eq. (25)]. It is of interest to compare the results of the exact calculations with approximate estimates. In the model of sudden switching of the exchange interaction, the effective radius of spin exchange between charged paramagnetic

Table 2 Values (in 10^{-8} cm units) of the effective radius of spin exchange between particles of like charge for a selected set of parameters of exchange and electrostatic interaction, and diffusion coefficient

J_0, rad/s	10^{10}				10^{11}				10^{12}				10^{13}			
æ, cm^{-1}	10^8		3×10^8		10^8		3×10^8		10^8		3×10^8		10^8		3×10^8	
D, cm^2/s	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}
$\varepsilon = 20$																
$r_D = 2A$	0.95	3.72	0.09	2.39	3.72	4.72	2.39	3.18	4.72	5.88	3.18	3.53	5.88	7.03	3.53	3.94
$r_D = 10A$	0.07	1.6	0.004	0.27	1.6	3.12	0.27	1.15	3.12	4.67	1.15	1.57	4.67	6.13	1.57	2.08
$\varepsilon = 81$																
$r_D = 2A$	1.08	3.75	0.12	2.57	3.75	4.73	2.58	3.25	4.73	5.88	3.25	3.58	5.88	7.03	3.58	3.97
$r_D = 10A$	0.59	3.22	0.05	1.77	3.22	4.33	1.77	2.67	4.33	5.58	2.67	3.04	5.58	6.81	3.04	3.48

The distance of the closest approach $r_0 = 6 \times 10^{-8}$ cm

particles is conventionally estimated as $r_{eff} = f\, P_{ex}\, r_0$ [see Eq. (21)] [2, 16]. In this expression, f is given by Eq. (12), and the efficiency of the spin exchange P_{ex} is given by Eq. (6), in which time τ is used as the effective collision time [Eq. (22)]. In this estimate, extended character of the exchange interaction is ignored, and it is considered that the exchange interaction is switched on suddenly only in a narrow layer between spheres with radii r_0 and $r_0 + \delta$. We studied to what extent the considered approximation is applicable for calculation of the effective radius of spin exchange between charged paramagnetic particles. Figure 6 shows the results of calculations according to formula $r_{eff} = f P_{ex} r_0$ and calculations using the consistent theory of spin exchange for particles of like charge and oppositely charged particles developed above.

It follows from Fig. 6 that the approximation $r_{eff} = f\, P_{ex} r_0$ Eq. (21) gives satisfactory values of the effective radius of the spin exchange between oppositely charged paramagnetic particles in nonviscous solution. In the case of opposite charges of colliding partners, the approximate results deviate noticeably only in viscous solutions with low diffusion coefficients and/or strong exchange integral (compare Fig. 6a–c). However, for particles of like charge it is seen (Fig. 6) that the approximation $r_{eff} = f P_{ex} r_0$ considerably underestimates the effective radius of the spin exchange. We interpret the last statement in the following way. When particles have like charge the Coulomb repulsion strongly reduces the collisions with the closest approach, $f_1 \ll 1$ [see Eq. (13)]. In this situation the exchange interaction at distances between particles more than the collision radius r_0 give an essential contribution to the spin exchange efficiency. This contribution is taken into account in the calculations using the consistent theory developed in this work and not when the approximation $r_{eff} = f P_{ex} r_0$ is used.

Thus the discrepancy between the effective spin exchange radii calculated in the framework of the consistent theory and in the framework of the sudden collision approximation arises due to an extended character of the exchange interaction [Eq. (9)].
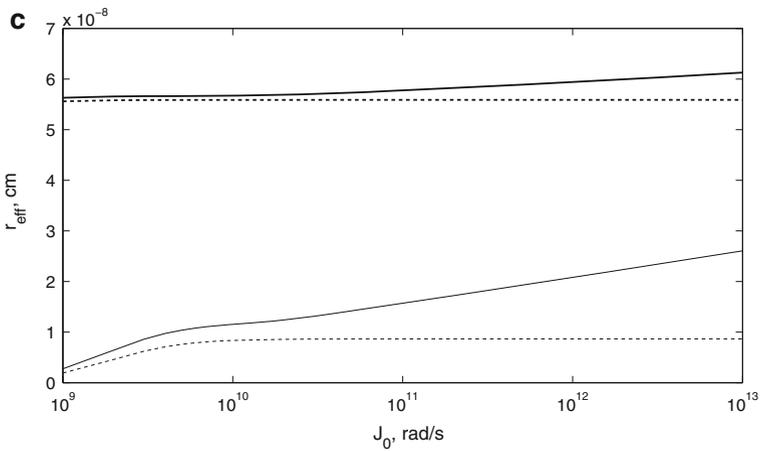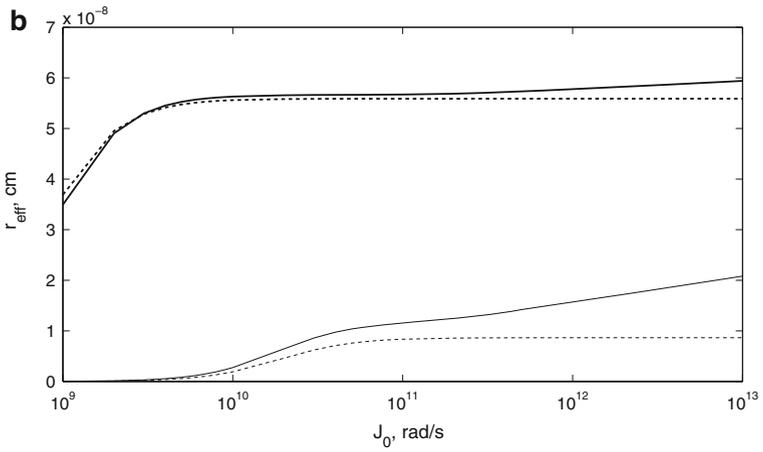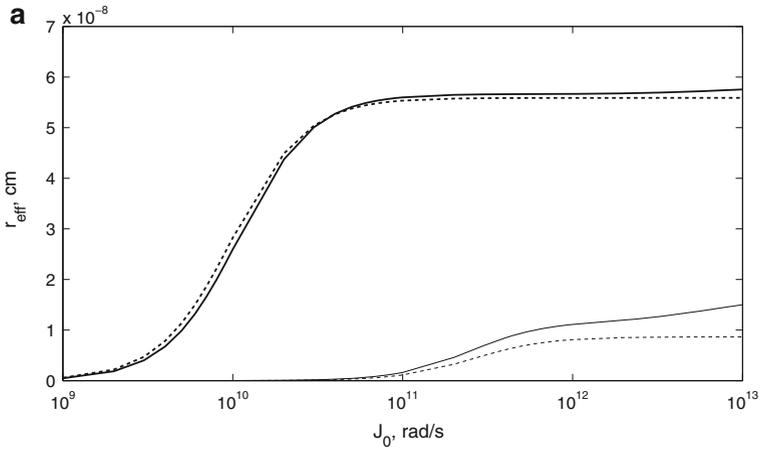
◄**Fig. 6** Comparison of the effective radius of the spin exchange calculated for oppositely charged particles (*thick curves*) and particles of like charge (*thin curves*) within the theory developed in this work (*solid curves*) and in the approximation $r_{eff} = f P_{ex} r_0$ (*dotted curves*). Calculations were performed for the following parameter values: $r_0 = 6 \times 10^{-8}$ cm, $\ae = 3 \times 10^8$ cm^{-1}, $\varepsilon = 20$, $r_D = 10^{-7}$ cm, $D_{AB} = 1.38 \times 10^{-5}$ cm^2/s (**a**), $D_{AB} = 10^{-6}$ cm^2/s (**b**), $D_{AB} = 10^{-7}$ cm^2/s (**c**)

3 Experimental Results and Discussion

Experimental results are taken from the literature [16]. The reader is referred to Ref. [16] for experimental details; here, we briefly summarize the methods and results.

The stable monoprotic nitroxide spin probe 2,2,5,5-tetramethylpyrrolidin-1-oxyl-3-carboxylic acid (3CP) was utilized as a model to study molecular collisions in aqueous electrolyte solutions. The rate constant of Heisenberg spin exchange, K_{ex}, for CP uncharged (at low pH) or charged (CP$^-$) (at high pH), was measured as functions of temperature and ionic strength. It will be instructive to compare the results for charged or uncharged 3CP with those of another relatively small, uncharged nitroxide spin probe (nitroxide), 2,2,6,6-tetramethyl-4-oxypiperidine-d$_{16}$ (pDT). By small, we mean that the unpaired spin density is sufficiently large over the entire molecule that the relative orientations of two nitroxides upon collision is unimportant. Contrast this with the situation in Ref. [7] where the nitroxide was not "small."
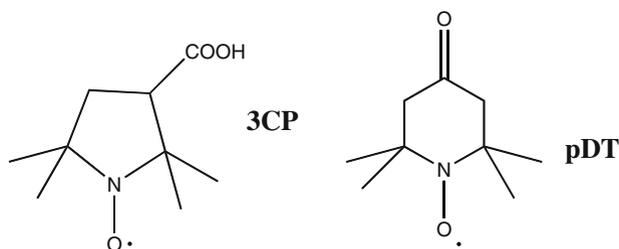
The concentration broadening, ΔB, in the EPR of 3CP, was studied in seven series of samples, each at constant ionic strength, four with 3CP$^-$ (Series A–D) and three with 3CP (Series E–G) varying the concentration of the nitroxide. The values of $2(C_{CP^-} + C_{NaCl} + C_{NaOH} + C_{HCl})$ were as follows (in mM): A, 67; B, 148; C, 297; D, 1,200; E, 29; F, 97; and G, 1,230. The results for 3CP were independent of ionic strength, so they were averaged over the three series. Either HCl or NaOH was added to shift the equilibrium between 3CP and 3CP$^-$ and NaCl was added to maintain the total ion concentration constant in each series. In all cases, ΔB was an excellent linear function of the concentration, C. The slopes of these lines in units G/M yield the values of K_{ex}.

Values of K_{ex} are given in column 7 of Table 3. The direct measurements of the spectra in Ref. [16] show that dipole–dipole contribution to the line width is negligible for all $T > 298$ K and contribute no more than 5 % at 298 K. The concentration broadening due to dipole–dipole interactions can be taken into account using methods developed recently [20, 21].

Table 3 Parameters and experimental results for aqueous 3CP and the effective radius of the spin exchange calculated numerically

Sample	ε^a	T	T/η T/cP cor. for NaCl	2 [ion]	$r_D/$ 10^{-8} cm	$<dBtot/$ $dC>^b$ G/M	r^c	$D_{AB},$ 10^{-5} cm^2/s	$r_{eff},$ 10^{-8} cm	æ = 3 × 10^8 cm^{-1}		æ = 2 × 10^8 cm^{-1}		æ = 5 × 10^8 cm^{-1}	
										r_{fitt} 10^{-8} cm	$J_0,$ 10^{11} rad/ s	r_{fitt} 10^{-8} cm	$J_0,$ 10^{11} rad/ s	r_{fitt} 10^{-8} cm	$J_0,$ 10^{11} rad/ s
A	78.4	298	333.80	0.067098	16.578	71.100	0.9990	1.514	1.420	1.421	1.126	1.420	0.694	1.420	2.005
A	73.2	313	477.81	0.067098	16.392	97.837	0.9990	2.168	1.364	1.364	1.564	1.364	0.966	1.364	2.782
A	68.3	328	647.97	0.067098	16.208	131.07	0.9990	2.938	1.348	1.348	2.123	1.348	1.310	1.348	3.775
A	63.8	343	844.45	0.067098	16.029	164.77	0.9999	3.829	1.301	1.301	2.703	1.301	1.671	1.301	4.801
A	59.5	358	1067.4	0.067098	15.854	203.07	0.9990	4.840	1.268	1.268	3.373	1.268	2.086	1.268	5.989
B	78.4	298	333.56	0.14788	11.167	73.353	0.9996	1.513	1.466	1.466	1.021	1.467	0.633	1.466	1.812
B	73.2	313	477.42	0.14788	11.041	103.50	0.9997	2.165	1.445	1.446	1.454	1.445	0.900	1.445	2.578
B	68.3	328	647.40	0.14788	10.918	140.20	0.9999	2.936	1.443	1.443	1.987	1.444	1.230	1.443	3.526
B	63.8	343	843.65	0.14788	10.797	179.30	0.9999	3.826	1.417	1.417	2.565	1.417	1.588	1.417	4.549
B	59.5	358	1066.3	0.14788	10.679	220.53	0.9998	4.835	1.379	1.379	3.184	1.379	1.972	1.379	5.644
C	78.4	298	331.29	0.29690	7.8812	80.000	0.9994	1.502	1.610	1.610	0.981	1.609	0.608	1.610	1.739
C	73.2	313	473.82	0.29690	7.7924	111.17	0.9998	2.149	1.564	1.564	1.369	1.565	0.850	1.564	2.425
C	68.3	328	642.11	0.29690	7.7053	146.93	0.9996	2.912	1.525	1.525	1.819	1.526	1.130	1.525	3.218
C	63.8	343	836.30	0.29690	7.6200	188.53	0.9998	3.792	1.503	1.503	2.348	1.503	1.458	1.503	4.153
C	59.5	358	1056.5	0.29690	7.5366	231.30	0.9997	4.791	1.459	1.459	2.897	1.459	1.801	1.459	5.120
D	78.4	298	318.19	1.1991	3.9216	90.827	0.9993	1.443	1.903	1.904	0.868	1.902	0.540	1.903	1.531
D	73.2	313	453.07	1.1991	3.8774	125.27	0.9999	2.055	1.843	1.844	1.192	1.844	0.744	1.843	2.100
D	68.3	328	611.82	1.1991	3.8340	169.17	0.9991	2.774	1.843	1.843	1.610	1.844	1.005	1.843	2.837
D	63.8	343	794.32	1.1991	3.7916	214.73	0.9999	3.602	1.802	1.802	2.040	1.803	1.275	1.802	3.592
D	59.5	358	1000.5	1.1991	3.7501	264.87	0.9998	4.537	1.765	1.765	2.514	1.765	1.572	1.765	4.423
E–G	78.4	298	334.79	0.025060	27.127	122.51	0.9980	1.518	2.439	2.439	1.049	2.439	0.651	2.439	1.861

Table 3 continued

Sample	ε[a]	T	T/η T/cP cor. for NaCl	2 [ion]	r_D, 10^{-8} cm	$<dBtot/dC>$[b] G/M	r[c]	D_{AB}, 10^{-5} cm^2/s	r_{eff}, 10^{-8} cm	æ = 3 × 10^8 cm^{-1}		æ = 2 × 10^8 cm^{-1}		æ = 5 × 10^8 cm^{-1}	
										r_{fitt}, 10^{-8} cm	J_0, 10^{11} rad/s	r_{fitt}, 10^{-8} cm	J_0, 10^{11} rad/s	r_{fitt}, 10^{-8} cm	J_0, 10^{11} rad/s
E–G	73.2	313	479.39	0.025060	26.822	170.91	0.9999	2.174	2.377	2.377	1.441	2.377	0.897	2.377	2.549
E–G	68.3	328	650.28	0.025060	26.522	225.54	0.9999	2.949	2.312	2.312	1.874	2.313	1.170	2.312	3.304
E–G	63.8	343	847.67	0.025060	26.228	280.67	0.9997	3.844	2.207	2.207	2.286	2.207	1.433	2.207	4.016
E–G	59.5	358	1071.7	0.025060	25.941	332.57	0.9996	4.860	2.069	2.069	2.659	2.069	1.674	2.069	4.650

[a] Data from Ref [23]

[b] Data from Ref. [16]

[c] Coefficient of correlation for linear fit versus the concentration

The translational diffusion coefficient of a sphere of radius a is often approximated by the Stokes–Einstein equation as follows:

$$D = kT/(6\pi a\eta) \tag{45}$$

where η is the shear viscosity. In the case of like molecules the mutual diffusion coefficient is twice the value given by Eq. (45). Values of the mutual diffusion coefficients for the systems studied are tabulated in column 9 of Table 3. In the theory we present the spin exchange rate constant as $K_{ex} = 4\pi r_{eff}D_{AB}$ From experimental data, we obtain this rate constant. Thus, from equation

$$4\pi \, r_{eff}D_{AB} = (3\sqrt{3}/4)\gamma dB/dC \tag{46}$$

we determine the experimental value of the spin exchange effective radius r_{eff}. The results are tabulated in column 10 of Table 3.

According to the theory of strong electrolytes [14], the thickness of the ionic layer (Debye screening radius), r_D, is defined by

$$r_D^{-2} = \frac{e^2}{\varepsilon_0 \varepsilon_r kT} \sum n_i Z_i^2 \tag{47}$$

where n_i is the number density of ions of type i with charge eZ_i. Evaluating the constants and changing units,

$$r_D^{-2} = \frac{1,265}{\varepsilon_r T} \sum C_i Z_i^2 = \frac{1,265}{\varepsilon_r T} 2(C_{CP^-} + C_{NaCl} + C_{NaOH} + C_{HCl}) \tag{48}$$

where r_D is given in Å with concentration of the ith ionic species and C_i, in mol L^{-1}. The second equality in Eq. (48) follows because only univalent ions are involved.

Utilizing data [22] for the temperature dependence of ϵ_r of water in the range 273–373 K, the r_D values for the samples are tabulated in column 6 of Table 3.

Figure 7 compares the temperature dependence of K_{ex} for 3CP and 3CP$^-$ with that for pDT. The viscosity of the solutions were corrected for the presence of salts using the equations of ref. [23]. Most of the viscosity correction, which reaches a maximum of 7 % at $C_{NaCl} = 600$ mM, is due to NaCl. Including all ions in the correction, using C_{total} rather than C_{NaCl} would only change the viscosity by a maximum of 0.6 %

The data presented on Table 3 allow us to make several observations.

The spin exchange rate constant and the effective radius of the spin exchange between radicals of like charge, 3CP$^-$, are less than between uncharged radicals, 3CP. This observation is rather trivial, since it is expected that Coulomb repulsion between 3CP$^-$ will reduce a probability of an encounter of the radicals of like charge compared to the case of uncharged radicals.

The spin exchange rate constant between charged radicals, 3CP$^-$, or uncharged, 3CP, radicals increases when the molecular diffusion coefficient (mobility of molecules) increases. This experimental fact is expected, since the diffusion coefficient determines the frequency of binary collisions [see, e.g., Eqs. (7, 8)].
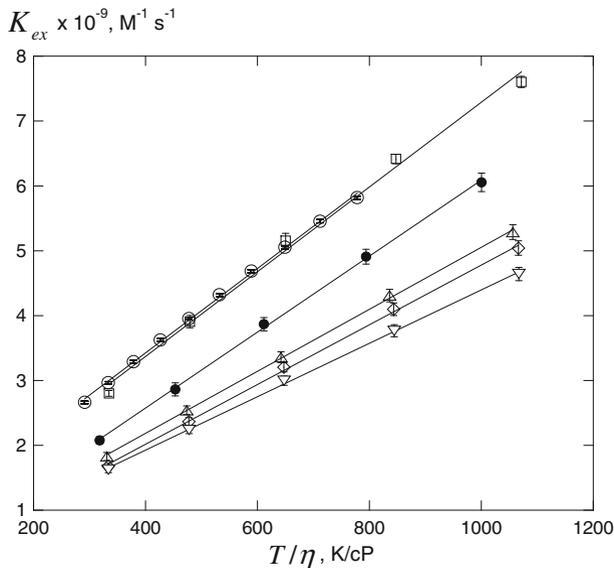
$K_{ex} \times 10^{-9}$, $M^{-1} s^{-1}$

Fig. 7 Spin exchange rate constants for Samples A *upside down triangles*, B *diamonds*, C *triangles*, D *filled circles,* Average E–G *squares*, data taken from ref. [16]; pDT, *open circles*, data taken from ref. [24]. The *lines* are linear least-squares fit to guide the eye. In this range DD is negligible for all samples. At lower temperatures, DD becomes significant for pDT and the corrected values of K_{ex} curve downward and extrapolate to the origin [24]. See Fig. 9 of ref. [24]

The effective radius of the spin exchange decreases when the diffusion coefficient increases (see column 7 in Table 3). This experimental observation supports the theoretical prediction. As was discussed in the Sect. 2 above, an increase of the molecular mobility reduces the time that two colliding particles spend in a region of their effective interaction.

Thus, the experimental data presented confirm qualitatively the theoretical predictions concerning the rate of the spin exchange between charged and uncharged paramagnetic particles.

However, when interpreting the experimental data quantitatively the theory meets difficulties. For the system considered in this section of our work, we know all molecular-kinetic parameters as well as parameters of an electrolyte. But we know very little about the magnitude of the exchange integral and the dependence of the exchange integral on a distance between two radicals in a solution. We wanted to determine the parameters of the exchange interaction by comparison of the effective radius of the spin exchange, found from the experimental data taken from [24] (column 10 in Table 3) and theoretical simulations with fitting parameters of the exchange interaction. Results of some simulations are presented in columns 11–16 in Table 3. In Table 3 we present the results of fitting for three different values of the parameter æ. For each chosen value of æ, we succeeded in finding fitting parameter J_0, which allows us to describe perfectly experimental data at 298 K. But the fitting parameter J_0 increases when the diffusion coefficient increases (see columns 11–16 in Table 3). We plan to investigate this observation further.

From Table 3 we see that the effective radius of the spin exchange, r_{eff}, is less than one-half of the collision radius, $r_0/2 = a = 3.23 \times 10^{-8}$ cm, $r_{eff} < a$ (see column 10 in Table 3). Thus for 3CP and 3CP$^-$ radicals, the spin exchange is not strong. From this fitting procedure we find that, in a case of 3CP, 3CP$^-$ radicals, the exchange integral at the closest approach of two radicals J_0 is around 10^{11} rad/s.

Our estimates of the two previous paragraphs rely quantitatively on the validity of the Stokes–Einstein equation that is known to be inaccurate in some cases. Particularly, in water, values of K_{ex} are consistently found to be smaller than in other solvents, by a factor of 0.50–0.71, attributed to a steric factor due to hydrogen bonding to the nitroxide. See ref. [25], and references therein. Thus, these estimates are presented to illustrate the method and more accurate values of J_0 and æ could result from a better understanding of the steric factors and the values of D_{AB}.

4 Conclusions

In this work we have developed a consistent theory of the bimolecular Heisenberg spin exchange between charged spin ½ paramagnetic particles in dilute solutions. There were formulated kinetic equations for the spin density matrices of the paramagnetic particles taking into account the binary collisions. The algorithm was suggested which allows one to determine numerically the rate constant and the effective radius of the spin exchange. For model situations there were investigated dependencies of the effective radius of the spin exchange on the molecular diffusion coefficient, on parameters of the Heisenberg exchange interaction and on the parameters which characterize the electrostatic interaction of the charged particles in electrolytes. The theory was applied for the analysis of the experimental data from literature for the radicals of like charge. Good qualitative agreement was achieved.

Within the proposed theory, the effective radius of the spin exchange of charged particles is determined by the parameters of the exchange interaction, $\{J_0, æ\}$, parameters of the electrostatic interaction, {dielectric permittivity ε, Debye screening radius r_D}, the collision radius r_0 and the coefficient of mutual diffusion of particles D_{AB}. The effective radius of the spin exchange $r_{eff}(J_0, æ, \varepsilon, r_D, r_0, D_{AB})$ can be calculated using the theory developed in this work if values of all parameters $\{J_0, æ, \varepsilon, r_D, r_0, D_{AB}\}$ are given. The spin exchange rate $K_{ex} = 4\pi r_{eff} D_{AB} C_B$ is measured in EPR experiments. Thus, the spin exchange rate measured in EPR experiments contains information about the interactions between paramagnetic particles, kinematics of the mutual diffusion of colliding pairs of paramagnetic particles and the local concentration C_B of paramagnetic particles. In such situation different strategies of the application of EPR spectroscopy are implemented when studying the spin exchange.

Let us assume that there is a system, for which all parameters, which determine K_{ex}, except for the exchange interaction parameters are known from some experiments. In this case, one can determine the effective radius of the spin exchange from the EPR data and then to select such values of the exchange integral parameters, which lead to the coincidence of the calculated radius of the spin exchange with the value for this radius found from data of EPR spectroscopy. As a

result, from data on the spin exchange in solutions one obtains information about the exchange interaction between two paramagnetic particles colliding in a solution. In this work, we have followed this strategy and estimated the exchange interaction parameters by using the rate constant of the spin exchange subtracted from the EPR data. The exchange integral depends on the overlap of electron orbitals, so that information about the exchange interaction obtained in this manner is useful in the analysis of the kinetics of the electron transfer during the binary collisions in a solution [2, 13].

The problem of determining the concentration of paramagnetic particles in complex systems may arise. For example, in some situations it is necessary to determine the concentration of oxygen molecules in certain regions of an organism. Collisions of spin probes with oxygen molecules broaden the EPR spectra lines of spin probes. One can find the oxygen concentration from the measured concentration broadening of the EPR lines, if there is a theoretical estimate of the effective radius of the spin exchange. Such a strategy of finding the concentration of paramagnetic particles agents broadening the EPR spectra lines of spin probes is quite successfully used in oximetry (see, e.g., [26]).

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