

# New Kinetic Equations for Spin-Dependent Recombination of Radical Pairs and Their Comparison with Existing Phenomenological Equations

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**Abstract:** For the first time, well-founded new kinetic equations for the density matrix of an ensemble of non-interacting radical pairs (RPs) are derived considering their spin-dependent recombination. Recombination of RP is considered as a quasi-unimolecular process. Similar to Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular reactions it is suggested that there is stochastic Poisson process which provides randomly chances for recombination. Those chances appear independent of a spin state of RPs. Whether the chance to recombine will be realized or not depends on the state of the spins of the unpaired electrons of the RPs. For this model the spin density matrix  $\rho(t)$  can be represented as the product of the RP density matrix (hypothetical pair)  $\rho^0(t)$ , in which the recombination of radicals is not included, and the probability  $f(t)$  that the RP in the time interval  $(0, t)$  survived, i.e. did not recombine:  $\rho(t)=f(t) \rho^0(t)$ . In this work, new kinetic equations for  $f(t)$  and  $\rho(t)$  are derived. The equation for  $f(t)$  gives in fact kinetic equations for the concentration of RPs. The basic equations are obtained for the situation when all RPs of the ensemble start in the same pure quantum state. The obtained kinetic equations are generalized to the case when the initial state of the system is mixed. For some set of parameters of RPs, results of new kinetic equations presented in this work were compared with results of existing phenomenological kinetic equations. While they correspond qualitatively, there is significant quantitative difference.

**Keywords:** Spin Chemistry, New Kinetic Equations, Kinetics of Radical Pairs Recombination, Spin-Dependent Recombination, Radical Pairs

## 1. Introduction

There are many examples of spin-dependent processes that occur between a pair of paramagnetic particles (see [1]). The most important example is the recombination of geminate radicals to form a diamagnetic product. In the overwhelming majority of cases, a pair of radicals recombines and gives a diamagnetic molecule only when the unpaired electrons are in a singlet state with a total spin of zero. A remarkable example is the pair of separated charges (radical ions), which are formed at the primary stage of photosynthesis. Another good example is the delayed fluorescence of organic molecules induced by triplet-triplet annihilation of excitons in molecular crystals (see, for example, [2-4]).

For a quantitative theory of magnetic and spin effects in spin-dependent processes, it is necessary to include in the equations for the spin density matrix of the pair of paramagnetic particles (for example, a pair of free radicals or a pair of triplet excitons) terms that describe the “loss” of pairs by reaction.

In order to simplify further discussions, let us focus on the recombination of radical pairs (RP), which is easily generalized to other cases.

At time  $t$ , let the spin state of the RP ensemble be described as a quantum superposition of the singlet and triplet states of the spins of unpaired RP electrons with the total projection of spins on the quantization axis equal to zero:

$$\Psi(t) = a(t) \psi_S + b(t) \psi_{T0}. \quad (1)$$

In terms of the density matrix in the basis  $\{S, T0\}$  states (1) corresponds to the matrix.

$$\rho(t) = \begin{pmatrix} a(t)^2 & a(t)b^*(t) \\ a^*(t)b(t) & b(t)^2 \end{pmatrix} \quad (2)$$

Let us assume that in the singlet state RPs can recombine. Phenomenologically, this can be taken into account by introducing an additional factor  $\exp(-Ks t/2)$  into the amplitude of the singlet contribution  $a(t)$  in (1). Then the RP population in the singlet state decreases as  $\exp(-Ks t)$  due to recombination. Within the framework of such a phenomenological approach, off-diagonal matrix elements decrease as  $\exp(-Ks t/2)$ , and the RP population in the triplet state does not change. Within the framework of this phenomenological approach, the contribution of the RP recombination to the equation for the density matrix can be written in the following compact form [5–7].

$$(\partial \rho / \partial t)_{\text{rec}} = - (Ks/2) (P_s \rho + \rho P_s). \quad (3)$$

In this equation,  $P_s$  is the projection operator into the subspace of the singlet state,  $P_s = |S\rangle\langle S|$ .

Along with (3), other options for describing the contribution of spin-dependent recombination to the equation for the RP spin matrix were also proposed (see, for example, [7–14]). In all cases when recombination occurs only for RP in the singlet state, the same equations are proposed for the RP populations in the singlet and triplet states, which also coincide with equations (3)

$$(\partial \rho_{ss} / \partial t)_{\text{rec}} = - Ks \rho_{ss}; \quad (4)$$

$$(\partial \rho_{T0T0} / \partial t)_{\text{rec}} = 0.$$

The proposals up to now differ from each other only for the off-diagonal elements of the spin density matrix.

In the case of equations (3), it is proposed [5–7].

$$(\partial \rho_{ST0} / \partial t)_{\text{rec}} = - (Ks/2) \rho_{ST0}. \quad (5)$$

In [11, 12], instead of (3), another equation was proposed.

$$(\partial \rho / \partial t)_{\text{rec}} = - Ks P_{T0} \rho P_{T0}; \quad (6)$$

In equation (6),  $P_{T0}$  is the projection operator into the triplet ( $T_0$ ) spin subspace. According to (6), for the diagonal elements of the density matrix, exactly the same equations (4) that give us equations (3) take place. For off-diagonal elements of the density matrix (6) gives a 2-fold faster decoherence of spin states compared to (3, 5).

$$(\partial \rho_{ST0} / \partial t)_{\text{rec}} = - Ks \rho_{ST0}. \quad (7)$$

In some cases, it is proposed to introduce a phenomenological constant,  $K$ , of the relaxation rate of the off-diagonal elements of the density matrix and write the phenomenological equations for spin decoherence in the form [7, 15].

$$(\partial \rho_{ST0} / \partial t)_{\text{rec}} = - K \rho_{ST0}. \quad (8)$$

The rate constant  $K$  in (8) includes not only decoherence due to RP loss both in Eqs. (5, 7) but also decoherence due to paramagnetic relaxation. We note that, in principle, spin-lattice paramagnetic relaxation should also be taken into account when writing the kinetic equations for the populations of spin states [1, 15]. The theory of paramagnetic relaxation of spins is well developed, and it allows one to include paramagnetic relaxation as an additive contribution to the kinetic equations for the RP density matrix (see, for example, [1, 15]).

Let us note a common property of all the kinetic equations for RP available in the literature for the spin-dependent recombination of pairs. They are all linear equations in the density matrix elements. What is also common to all equations (3–6) is that they are written just by hand, they are not derived consistently within the framework of a clearly formulated recombination model of RPs. Indeed, the introduction of an additional decrease in the amplitude of the contribution of the singlet state to the wave function (1) is, to put it mildly, a strange procedure. In fact, when a particular pair of radicals recombines, this pair simply disappears, and accordingly, no wave function of it remains. If, in a pure quantum state, the superposition of a singlet and a triplet recombines to the extent of the singlet's contribution, then this does not mean that nothing changes in the population of the triplet state. The act of recombination that took place “knocks out” individual RP from the ensemble, along with their populations and quantum coherences.

In this paper, we propose a different approach to describe the behavior of the RP density matrix with allowance for recombination. First, the RP recombination model is presented. Then, for this model, we obtain the kinetic equations for the RP density matrix. The results are compared with the solutions obtained using equations (3) and (6).

## 2. RP Recombination Model

The recombination of two radicals is a bimolecular reaction. This implies that the radicals approach each other in the course of random movements and can give a recombination product. But the recombination of a given pair of radicals is essentially a unimolecular process (in chemical kinetics, such processes are called quasi-unimolecular). The kinetics of unimolecular processes, for example, the thermal dissociation of molecules with concentration  $C$ , in accordance with the law of mass action, is described by the equation.

$$\partial C / \partial t = -k C. \quad (9)$$

Such kinetics can be theoretically derived from the assumption that unimolecular dissociation is a Poisson process that is uniform in time. According to the quasi-equilibrium RRKM theory of unimolecular reactions, an elementary act of dissociation or isomerization occurs when, as a result of a random redistribution of energy between the

vibrational and rotational degrees of freedom of the molecule, conditions ("chance") for dissociation or isomerization arise [16]. The fact that the law of mass action (9) works in many cases indicates that the random Poisson process can serve as a good model in many cases. In the case where a pair of radical ions (cation and anion) recombines, recombination requires the transfer of an electron. According to the Marcus theory, the reorganization of the environment (a certain electric polarization) is necessary for electron transfer [16]. The reorganization of the medium in the course of the thermal motion of atoms randomly creates the necessary conditions ("chance") for electron transfer. And this process can be modeled using the Poisson process.

Let us assume that the RP ensemble is prepared in the singlet spin state and that the RP can only recombine in the singlet spin state. If we assume that singlet-triplet transitions do not occur and that RP recombination is a Poisson process uniform in time with a rate constant  $K_s$ , then to consider RP recombination, a term can be added to the equation for the density matrix (cf. (9)).

$$(\partial \rho / \partial t)_{\text{rec}} = -K_s \rho. \quad (10)$$

$K_s$ -rate constant of the quasi- unimolecular RP recombination reaction in the singlet spin state.

In fact, spin interactions cause singlet-triplet transitions. Therefore, the kinetics of RP recombination must somehow take into account the fact that, due to the spin dynamics of RP, it can turn out to be in situations where circumstances external to spins have created conditions favorable for recombination, but the spin state of the pair does not allow RP to recombine. Thus, the behavior of the RP is determined, on the one hand, by the Poisson process created by the motion of the degrees of freedom external to the spins, and, on the other hand, by the motion of the spins of unpaired electrons, which is determined by the spin Hamiltonian of the RP and the initial state of the spins of the pair of paramagnetic particles. In fact, the spin dynamics forms a "quantum random process" based on the spin selection rules for the RP recombination.

In this paper, we will consider a simple situation where the spin Hamiltonian of the pair and  $K_s$  have constant values that do not change with time. The results obtained under this assumption can be further generalized to situations with random modulation of the pair spin Hamiltonian parameters and the RP recombination rate constant.

### 3. Derivation of the Kinetic Equation for the RP Density Matrix Considering the Recombination of Radicals

When deriving the equations, we assume that recombination and spin interactions between radicals from different pairs can be neglected. They greatly complicate the problem without producing new features.

In the absence of radical recombination, the dynamics of the spins is given by

$$\partial \rho^0 / \partial t = - (i/\hbar) [H, \rho^0]. \quad (11)$$

Here  $H$  is the RP spin Hamiltonian, the density matrix has index zero. This is done in order to emphasize that the density matrix found from solution (11) refers to a hypothetical pair in which all the processes that occur in real pairs occur, with the exception of pair recombination. The pair density matrix with allowance for recombination will be denoted as  $\rho$  without index. It is important to emphasize that at the initial moment of time both ensembles, hypothetical and real, are given by the same density matrix.

$$\rho_0(0) = \rho(0). \quad (12)$$

For further considerations, it is extremely important to distinguish the nature of the initial state.

The initial state of pairs can be a quantum pure state, i.e. be a given quantum superposition of the basis states. In the case of RP recombination, the basis states are the singlet and triplet states of the RP spins. For example, in the primary photochemical act of charge separation in the reaction center of photosystems, radical ion pairs are born, and all of them are born in such a state in which the state of spins in all pairs is a singlet. If the initial state is a quantum superposition, the initial density matrix (12) can have non-zero off-diagonal matrix elements in the calculation basis, which we have chosen for the RP singlet and triplet states.

The initial state of the pairs can be a mixture of different states. For example, one fraction of the RP can be prepared in the singlet spin state, and the other fraction in the triplet spin state  $T_0$  with zero projection of the total spin of the RP. In the case of such a mixed initial state of the RP, the density matrix will have non-zero diagonal elements,  $\rho_{SS} \neq 0$ ,  $\rho_{T_0 T_0} \neq 0$ , but the off-diagonal matrix element is equal to zero,  $\rho_{ST_0} = 0$ . In a mixture of pairs, there is no quantum coherence inherent in a quantum superposition of states.

Taking into account the indicated differences between pure and mixed states, we will consider these cases separately.

#### 3.1. An Ensemble of Identical RPs Prepared in a Pure Quantum State

If the recombination of pairs is not considered, then the density matrix  $\rho^0(t)$  of such a hypothetical ensemble of pairs can be found by solving Eq. (11) with the initial condition (12).

Considering the RP recombination, within the framework of the described model, the desired spin density matrix  $\rho(t)$  can be represented as  $\rho(t) = f(t) \rho^0(t)$ . In this work, kinetic equations for  $f(t)$  and  $\rho(t)$  are obtained.

At any moment of time random RPs can recombine and "depart" from the RP ensemble. This means that by the time  $t$ , only a part of the RPs,  $f(t)$ , will remain that have avoided recombination. The density matrix of the subensemble of surviving RPs can be represented as the product of the density matrix of RPs (a hypothetical pair)  $\rho^0(t)$ , in which the recombination of radicals is excluded, and the probability  $f(t)$  that the RP in the time interval  $(0, t)$  survived (did not recombine):

$$\rho(t) = f(t) \rho^0(t). \quad (13)$$

The trace of the matrix  $\rho^0(t)$  is equal to 1. Therefore, for the  $j$ -th set of identical RPs,  $f_j(t) = \text{Tr}\{\rho_j(t)\}$ ,

$f_j(t)$  describes the RP recombination kinetics of the  $j$ -th set of identical RPs, and the kinetics of the number of RPs that escaped recombination.

In fact, the fraction  $f(t)$  that avoided RP recombination specifies a decrease in the normalization of the density matrix, i.e. sets the reduction in the number of pairs of particles. It is interesting to note that the RP decay kinetics can be found as the ratio of the corresponding matrix elements,

$$f(t) = \rho_{mn}(t) / \rho_{mn}^0(t). \quad (14)$$

Note, Equation (14) is valid only for a pure state of identical RPs with no relaxation.

This possibility may be useful if only one matrix element is observed in the experiment, for example, the fraction of RPs in the singlet state. Note that the population of states for a hypothetical ensemble can be calculated theoretically.

In this work, for the first time, the total probability  $f(t)$  that RP avoids recombination in the time interval  $(0, t)$  was calculated for the recombination model as a Poisson random process.

For definiteness, let us assume that RPs can only recombine in the singlet spin state.

As already noted, at time  $t$  the RP ensemble will consist only of those RPs that “survived” by this moment, despite the fact that they had a chance to recombine in the time interval  $(0, t)$ . Let us find the contributions of subensembles that have survived by the time  $t$  of observation of pairs of radicals for different numbers of chances to recombine.

For the Poisson process, the probability that during the time  $t$  there will be no chance for the RP to recombine is equal to  $f_0 = \exp(-K_s t)$ .

The contribution of the RP subensemble that survived despite having one chance to recombine can be found as the product of the probabilities of the two processes. Let's assume that this single chance falls on the time interval  $(t_1, t_1 + \Delta t_1)$ . Then for the Poisson process the probability of this chance is equal to  $\exp(-K_s t) K_s \Delta t_1$ . But this probability is not yet the probability of RP recombination that we are looking for. To recombine, the RP must be in the singlet state. The probability of RP to be in the reactive singlet state is equal to  $\rho_{ss}^0(t_1)$  and to be in non-reactive triplet state is equal to  $\rho_{TT}^0(t_1) = 1 - \rho_{ss}^0(t_1)$ . The probability of RP to avoid recombination in the time interval  $(t_1, t_1 + \Delta t_1)$  is equal to  $\exp(-K_s t) K_s \Delta t_1 (1 - \rho_{ss}^0(t_1))$ . Summing up the contributions over the entire time interval, we finally obtain the probability for the survival of the RP under the condition that in the interval  $(0, t)$  there was the only one chance for recombination,

$$f_1 = \exp(-K_s t) \int_0^t dt_1 K_s (1 - \rho_{ss}^0(t_1)).$$

Similar reasoning gives the probability of RP survival under the condition that there were two chances for recombination in the interval  $(0, t)$ ,

$$f_2 = \exp(-K_s t) \int_0^t K_s (1 - \rho_{ss}^0(t_2)) dt_2 \int_0^{t_2} K_s (1 - \rho_{ss}^0(t_1)) dt_1.$$

Summing up the contributions of all RP subensembles that correspond to a different number, from zero to infinity, chances for recombination in the interval  $(0, t)$ , for the total probability of RP to avoid recombination and survive, we get

$$f(t) = \exp(-K_s t) \{1 + \int_0^t dt_1 K_s (1 - \rho_{ss}^0(t_1)) + \int_0^t dt_2 K_s (1 - \rho_{ss}^0(t_2)) \int_0^{t_2} dt_1 K_s (1 - \rho_{ss}^0(t_1)) + \dots\}. \quad (15)$$

It turns out that this infinite sum can be found. To do this, we need to take the derivative  $f(t)$  (15) of time. It turns out a linear differential equation.

$$\partial f(t) / \partial t = -K_s \rho_{ss}^0(t) f(t). \quad (16)$$

The function  $f(t)$  by definition (15) describes the proportion of survivors by the time of RP observation. Therefore, (16) can be considered as a kinetic equation for the RP concentration.

From equation (16) we get

$$f(t) = \exp(-K_s \int_0^t dt \rho_{ss}^0(t));$$

$$\rho(t) = f(t) \rho^0(t) = \exp(-K_s \int_0^t dt \rho_{ss}^0(t)) \rho^0(t). \quad (17)$$

Using (11, 13, 17), we obtain the kinetic equation for the RP density matrix with allowance for recombination for the situation when RPs recombine in the singlet state and at the initial moment all RPs are in a given pure quantum state,

$$\partial \rho(t) / \partial t = - (i/\hbar) [H, \rho(t)] - K_s \rho_{ss}^0(t) \rho(t). \quad (18)$$

The last results can be generalized to other cases. If RP recombination can occur not only in the singlet, but also in the triplet state, then instead of (18) we obtain the equation

$$\partial \rho(t) / \partial t = - (i/\hbar) [H, \rho(t)] - (K_s \rho_{ss}^0(t) + K_T \text{Tr}\{P_T \rho^0(t) P_T\}) \rho(t). \quad (19)$$

In this equation,  $K_T$  is the RP recombination rate constant in the triplet state, the  $P_T$  is operator of projection into the triplet subspace of the RP spin states,  $\text{Tr}\{\}$  gives the total population of the RP triplet states. When deriving (19), it was assumed that, in any of the triplet spin states, RP recombination occurs with the same rate constant  $K_T$ .

The proportion of RP that avoided recombination in this case is equal to

$$f(t) = \exp[-\int_0^t dt (K_s \rho_{ss}^0(t) + K_T \text{Tr}\{P_T \rho^0(t) P_T\})]. \quad (20)$$

To concretize the results obtained, we consider a specific model system.

Let us assume that the paramagnetic relaxation does not have time to noticeably manifest itself during the lifetime of the RP and, therefore, we do not take into account the paramagnetic relaxation in model calculations.

Let RP be given with the spin Hamiltonian

$$H = \omega_A S_{Az} + \omega_B S_{Bz}. \quad (21)$$

Let us assume that the RP ensemble is prepared in the singlet spin state.

Then at time  $t$  the elements of the density matrix RP in the  $S$ - $T_0$  basis are equal to

$$\begin{aligned}\rho_{SS}^0(t) &= \cos^2((\omega_A - \omega_B)t/2); \\ \rho_{TOT0}^0(t) &= \sin^2((\omega_A - \omega_B)t/2); \\ \rho_{ST0}^0(t) &= (i/2)\sin((\omega_A - \omega_B)t); \\ \rho_{T0S}^0(t) &= (-i/2)\sin((\omega_A - \omega_B)t);\end{aligned}\quad (22)$$

If we assume that RPs recombine only in the singlet state, from equations (17, 22) we obtain the fraction of RPs that avoided recombination in the form

$$f(t|S) = \exp[-(K_S/2) (t + (1/(\omega_A - \omega_B)) \sin((\omega_A - \omega_B)t))]. \quad (23)$$

If the RP ensemble were prepared in the triplet  $T_0$  state, then we would have

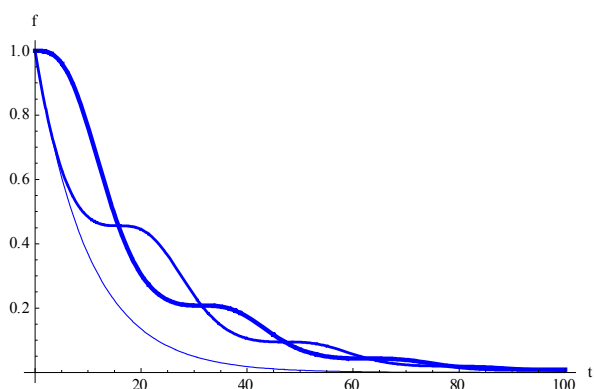
$$\rho_{SS}^0(t) = \sin^2((\omega_A - \omega_B)t/2).$$

Substituting this population value of the singlet state into (17), we obtain

$$f(t|T0) = \exp[-(K_S/2) [t - (1/(\omega_A - \omega_B)) \sin((\omega_A - \omega_B)t)]]. \quad (24)$$

Comparison of (23) and (24) specifically demonstrates the expected dependence of the fraction of RPs that escaped spin-selective recombination on the initial state of RP spins.

For clarity, Figure 1 shows the kinetic curves of the decrease in the amount of RP due to their recombination. They show that the kinetic curves really strongly depend on the initial state of the spins and on the frequency of singlet-triplet transitions.



**Figure 1.** Kinetic curves  $f(t)$  calculated from (23) for the singlet RP precursor (thin curve) and from (24) for the triplet precursor (thick curve). Calculation parameters:  $K_S=0.1$ ;  $\omega_B - \omega_A=0.2$ . A very thin curve depicts the function  $\exp(-K_S t)$ .

For comparison, Figure 1 shows the RP recombination kinetics if singlet and triplet pairs recombine with a rate constant equal to  $K_S=0.1$  (very thin lower curve in Figure 2). RP oscillations between the singlet state, in which RP can recombine, and the triplet nonreactive state significantly delays the recombination of radicals.

When RP recombination can occur both in the singlet and triplet  $T_0$  states and the RP ensemble starts in the singlet state of spins, from (20, 22) we obtain

$$f(t) = \exp[-[K t + (\Delta K/(\omega_A - \omega_B)) \sin((\omega_A - \omega_B)t)]]. \quad (25)$$

$$\text{Here } K = (K_S + K_T)/2, \Delta K = (K_S - K_T)/2.$$

Note that for  $K_S = K_T = K$ , i.e. with the same reactivity for all RP spin states, equation (25) gives the result expected for the Poisson recombination process (see (10)).

$$\rho(t) = f(t) \rho^0(t) = \exp(-K t) \rho^0(t). \quad (26)$$

The results obtained above show that the spin state of a pair of radicals manifests itself in their recombination qualitatively similarly to the manifestation of the steric factor in chemical reactions. True, in contrast to the steric factor, the influence of spin selection is not described by some constant coefficient. This coefficient oscillates over time.

There is one important feature of equations (18, 19). The contribution of recombination in a sense turns out to be a quadratic function of the RP density matrix, since the product of the density matrix element without recombination by the RP density matrix with allowance for the recombination of radicals appears in them. This fact must be taken into account when analyzing the RP ensemble in a mixed state.

### 3.2. An Ensemble of RPs Prepared in a Mixed State

Above, the kinetic equations for the spin density matrix were obtained for RP ensembles prepared in pure quantum states. In this case, all RPs are identical. An ensemble in a mixed state is a mixture of subensembles, each of which, with a given probability, is in one of the pure quantum states that make up the computational basis. For example, in the case of RP, we use the singlet and triplet spin states as a computational basis.

For mixed states, the total RP density matrix, considering the recombination of radicals, can be found as follows. Let us assume that we are given an ensemble of RPs in which the fraction of pairs  $w_1$  is prepared in the singlet state, and the fraction of pairs  $w_2=1-w_1$  is prepared in the triplet state.

The density matrix of the entire ensemble is the sum of the density matrices of the subensembles calculated with the given statistical weights  $w_1$  and  $w_2$ . Let us assume that RPs recombine only in the singlet state. Then the kinetic equation (18) is solved separately for the above subensembles. For both subensembles, we solve an equation of the form (18), but for each subensemble it is necessary to use the initial conditions inherent in them and the populations of the states  $\rho_{SS}^0(t)$  and  $\rho_{TOT0}^0(t)$  corresponding to these initial conditions. Such a separate calculation for each subensemble has to be done because the kinetic equations (18) are not linear.

For example, for the case considered above, when transitions from the singlet state to one triplet state  $T_0$  occur in the RP, under the assumption that the RP recombination occurs only in the singlet state, the fraction of pairs that avoided recombination is equal to

$$f(t) = w_1 \exp(-Ks \int_0^t dt \cos^2((\omega_A - \omega_B)t/2)) + w_2 \exp(-Ks \int_0^t dt \sin^2((\omega_A - \omega_B)t/2)). \quad (27)$$

### 3.3. Comparison of Numerical Results Obtained Using New and Existing Phenomenological Kinetic Equations

The existing theories of the spin-dependent RP recombination kinetics are phenomenological. In some form, they include the dependence of the RP recombination on the total spin of the unpaired electrons of the pair. And now, for more than half a century, they have been helping to interpret experimental data on spin chemistry. At the same time, in these phenomenological theories there is no clearly formulated idea for describing quantum coherence in the state of RP spins in the presence of recombination of radicals in a pair.

In this work, a different approach was used. First, a clear model of RP recombination was formulated considering the effect of spins on recombination, and then, within the framework of this model, the kinetic equation for the RP density matrix was found in a consistent manner. In particular, a kinetic equation for the RP concentration was found.

Therefore, it is of great interest to compare the results of two different approaches. For this purpose, the same quantities were calculated using different kinetic equations for the RP density matrix. For different values of the RP parameters, for example, the populations of the singlet and triplet states of the RP ensemble were calculated.

For definiteness, we assume that a pair of radicals recombine only in the singlet spin state. Among the existing theories, for comparison with the results of this work, there have been selected well-known Eqs. (3) [5-7] (note that we

neglected the contribution of paramagnetic relaxation)

$$\partial \rho(t)/\partial t = - (i/\hbar)[H, \rho(t)] - (Ks/2) (P_s \rho(t) + \rho(t) P_s) \quad (28)$$

and equations (cf. (6), [11, 12])

$$\partial \rho(t)/\partial t = - (i/\hbar)[H, \rho(t)] - Ks P_{T0} \rho P_{T0}. \quad (29)$$

These equations were compared with equations (see (18)) proposed in this work:

$$\partial \rho(t)/\partial t = - (i/\hbar)[H, \rho(t)] - Ks \rho_{ss}^0(t) \rho(t).$$

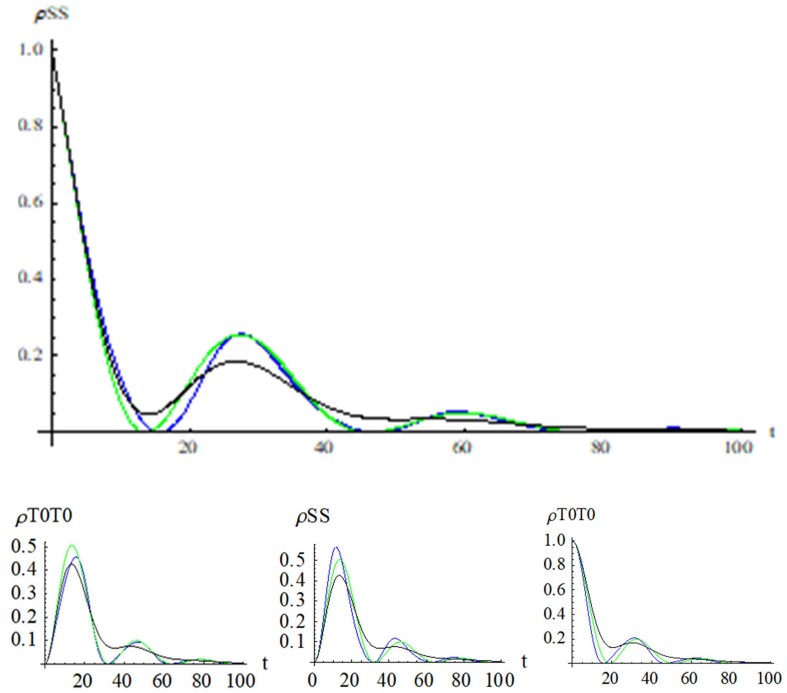
The above equations make it possible to calculate the RP density matrix taking into account spin-dependent recombination. They all solve the same problem. Equations (28) and (29) have much in common. They are both linear in the density matrix. They describe the decrease in the RP population in the singlet state in the same way. But they describe differently, first of all, the quantum coherence of the singlet and triplet states.

Equation (18) differs fundamentally from (28) and (29) in form. First, (18) turns out to be nonlinear in the density matrix. Second, according to (18), RP recombination equally changes all matrix elements, both diagonal elements (populations) and off-diagonal elements (quantum coherences).

To get an idea of the potential of different theories, numerical calculations of the population of the singlet and triplet states of the RP were carried out using equations (18, 28, 29).

The calculations were carried out for the simplest model described above, when the RP spin Hamiltonian has the form (21).

The results of numerical calculations are shown in Figure 2.



**Figure 2.** Time dependence of the populations of the singlet state,  $\rho_{SS}$ , and the triplet state,  $\rho_{TOT0}$ , for the singlet-born (upper curves) and the triplet-born (down curves) radical pairs. Blue lines are solutions of Eqs. (18) obtained in this work, green curves are solutions of Eqs. (28) and black curves are solutions of Eqs. (29). Parameters of calculations:  $Ks=0.1$ ;  $\omega_A-\omega_B=0.1$ .

A comparison of the curves in Figure 2 shows that the phenomenological kinetic equations (28, 29) and equation (18), obtained in this work in a consistent way for a model in which the RP recombination without considering the spin dependence of this reaction (the hypothetical spinless RP model) is time-homogeneous Poisson process, qualitatively give comparable results. This result seems to be quite expected, since when formulating the phenomenological equations, we tried to reflect important aspects of the relationship between the spin state of the RP and their recombination. The fact that the results of the phenomenological theories are qualitatively comparable with those of the consistent theory confirms that these phenomenological equations have been useful for evaluating magnetic and spin effects in spin chemistry.

Attention should be paid to the fact that quantitatively phenomenological theories predict results that differ significantly from the results of a consistent description of the kinetics of spin-dependent RP recombination proposed in this work.

We need experiments that could test quantitatively the predictions of different theories. For example, the theory proposed in this work predicts (see (14)) that for RPs prepared at the initial time in a pure quantum state, recombination equally reduces all elements of the density matrix in the S-T basis. Phenomenological theories predict quite different behavior.

It would be useful to analyze some of the already published experimental data, taking into account the results of the theory proposed in this paper. I would be glad to cooperate in such a matter.

## 4. Conclusion

In this work, for the first time, a kinetic equation for the spin density matrix of radical pairs was obtained in a consistent manner, consistently considering the spin-selective recombination of radicals in a pair.

The main idea of this work is as follows. In an ensemble of radical pairs (RPs), only a part of the RP actually recombines at any given time. Those pairs that recombine immediately drop out of the ensemble, and the number of pairs in the ensemble decreases. All RPs that escaped recombination in one way or another have density matrices unperturbed by recombination. Therefore, the task is to calculate the probability that the RP will avoid recombination by the time of observation. To solve this problem, it is necessary to set the RP recombination model. In this work, it is proposed to consider recombination as a Poisson process that is homogeneous in time. For this case, the problem is quite easy to solve. As a result, a kinetic equation for the RP density matrix was obtained taking into account the spin-dependent recombination of radicals in a pair (see (18, 19)). For example, in the case when only RPs in the singlet state can recombine, the contribution of recombination to the kinetic equation is

$$(\partial \rho(t)/\partial t)_{\text{rec}} = -K_s \rho_{\text{ss}}^0(t) \rho(t). \quad (30)$$

It should be emphasized that (30) was obtained under the assumption that the initial state of the RP is a pure quantum state. In the case of an RP ensemble in a mixed state, equations (30) must be solved for each of the RP subensembles in a purely quantum state that contribute to the mixed state (see (27)).

We note that (30) can be interpreted as the usual kinetic equation for unimolecular (quasi- unimolecular) reactions, if we consider  $K_s \rho_{\text{ss}}^0(t)$  as the instantaneous value of the “constant” of the reaction rate. It turns out that the singlet-triplet evolution of pair spins modulates the effective “constant” of quasi- unimolecular recombination of RP.

It is possible to formulate one of the necessary requirements for the form of kinetic equations for the density matrix of RPs, considering spin-dependent recombination. This requirement is that the kinetic equations should take the form of equations (10), if in the tested equations it is assumed that recombination does not depend on the state of electron spins, i.e. in both singlet and triplet states, the recombination rate constants coincide,  $K_T = K_S$ . It turns out that the kinetic equations proposed in this paper (see, for example, (18, 19)) fully satisfy this requirement. As for the phenomenological kinetic equations, only equations of the form (3, 28) satisfy this requirement. Indeed, if recombination of RPs is possible in both singlet and triplet spin states, equations (3, 28) are generalized to the form

$$\partial \rho(t)/\partial t = -(i/\hbar) [H, \rho(t)] - (K_S/2)(P_S \rho(t) + \rho(t) P_S) - (K_T/2)(P_T \rho(t) + \rho(t) P_T). \quad (31)$$

In the limiting case  $K_T = K_S$ , these equations turn into Eqs. (10).

However, the phenomenological approach proposed in [11, 12] (see Eqs. (6)), when generalized to the case of the possibility of recombination of RP in both singlet and triplet spin states, gives kinetic equations

$$\partial \rho(t)/\partial t = -(i/\hbar) [H, \rho(t)] - K_S P(t) \rho(t) + K_S (\rho(t) P_T) - K_T \rho(t) + K_T (P_S \rho(t) P_S), \quad (32)$$

which in the limiting case  $K_T = K_S$  are not reduced to Eqs. (10)

I am rather confident that the results of this work will give an additional impetus to the development of spin chemistry.

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