

# Time evolution of the spin state of the radical ion pair in the microwave field: an analytical solution

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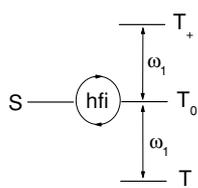
## Abstract

This paper reports an exact solution for the problem of spin evolution of a radical ion pair in a static magnetic and resonant a microwave field taking into account Zeeman and hyperfine interactions and spin relaxation. The values of parameters that provide one of the four possible types of solution are analysed. It is demonstrated that in the absence of spin relaxation, besides the zero field invariant an invariant at large amplitudes of the resonant microwave field can be found. The two invariants open the possibility for simple calculation of microwave pulses to control quantum state of the radical pair. The effect of relaxation on the invariants is analysed and it is shown that changes in the high field invariant are induced by phase relaxation.

## 1. Introduction

The problem of controlling elementary chemical reactions, and especially the advances in the field of quantum informatics [1], stimulates interest towards controlling the quantum state of microscopic spin systems [2]. Spin correlated radical pairs are one of the most intriguing quantum objects. The quantum state of such a pair can be controlled by applying external magnetic fields [3, 4]. Additional application of resonant microwave fields substantially widens the possibilities for manipulating the spins.

Figure 1 shows the scheme of transitions between spin states of a radical ion pair induced by hyperfine interaction with magnetic nuclei and resonant microwave field. Usually the set of singlet state of the pair  $|S\rangle$  with zero total spin and three triplet states  $|T_+\rangle$ ,  $|T_0\rangle$  and  $|T_-\rangle$  with total spin 1 and its projection on the  $z$  axis equal to +1, 0 and  $-1$ , respectively, is taken as the basis. In strong applied magnetic field the degeneracy of the triplet states is lifted by Zeeman interaction. In the absence of microwave field and relaxation the populations of  $|T_+\rangle$  and  $|T_-\rangle$  states, as well as the sum of the populations of  $|T_0\rangle$  and  $|S\rangle$  states remain constant. In the presence of hyperfine interaction the states  $|T_0\rangle$  and  $|S\rangle$  are not stationary, and their populations periodically change with time. This phenomenon is referred to as quantum beats and is observed in experiment [5, 6]. Quantum beats can also be induced by differences in the  $g$ -values of the pair partners [7].



**Figure 1.** Spin dynamics of a radical ion pair.

A resonant microwave field induces transitions between the triplet states, which leads to changes in the population of the singlet state of the pair and can be used to optically detect ESR spectra of radical ions in liquids [8, 9]. If the rate of transitions between  $|S\rangle$  and  $|T_0\rangle$  states is higher than between the triplet states, periodic changes of the singlet state population with frequency proportional to the amplitude of the microwave field are observed, which is referred to as quantum oscillations [10–12]. In the opposite limiting case of the strong microwave field, when the rate of transitions between the triplet states exceeds the rate of transitions between  $|S\rangle$  and  $|T_0\rangle$ , singlet-triplet transitions are slowed down, and the so-called spin locking is observed. As was demonstrated [13] for pairs formed in the singlet initial spin state a strong microwave field only slows down singlet-triplet transitions but does not completely block them, and the population of  $|T_0\rangle$  state always remains low. This was suggested as a possible route to control the spin state of such a pair. If the microwave field is switched off at the moment when the population of the singlet state is minimal, most pairs will be trapped in the  $|T_+\rangle$  and  $|T_-\rangle$  states. The only way to get into the singlet state for them is spin-lattice relaxation. A similar idea was exploited to experimentally substantially prolong the lifetime of the radical pair in photosynthetic reaction centre [14] by transferring it into its  $|T_+\rangle$  and  $|T_-\rangle$  states. Another route to control the spin state of the pair was found theoretically in the work [15]. If a strong resonant microwave field is rapidly switched on at the moment when the spin system is in its  $|T_0\rangle$  state, the pair is completely locked in the triplet state and will never become singlet through dynamic transitions. A possibility of controlling the spin state of the pair with very short pulses of very strong microwave field has also been treated theoretically [16]. The theory shows that quantum beats in the radical pair can be controlled with two (for singlet-born pairs) or just one (for triplet-born pairs) short microwave pulses.

The already cited works [13, 15] treated spin dynamics of a radical pair in static magnetic and resonant microwave fields neglecting relaxation. A method for solving the problem of spin dynamics, taking into account relaxation, was developed in work [12], and approximate solutions in the two limiting cases of large and small splitting were obtained. A method for numerical solution of this problem, taking into account relaxation and ion-molecular charge transfer reaction, was developed in work [17]. In the present contribution we provide a general analytical solution for the problem of spin evolution of a radical ion pair taking into account spin relaxation and use it to analyse the characteristic features of time evolution of the pair spin state in the microwave field.

## 2. Analytical solution

### 2.1. Model

Let us consider what happens when a non-polar solution is irradiated by ionizing radiation. As an example we shall use liquid hydrocarbons (RH), in which ionizing irradiation in the presence of electron (A) and hole acceptors (D) initiates the processes which in turn lead to the

formation of several types of singlet spin correlated pairs ( $\text{RH}\cdot^+/\text{e}^-$ ), ( $\text{RH}\cdot^+/\text{A}\cdot^-$ ), ( $\text{D}\cdot^+/\text{e}^-$ ) and ( $\text{D}\cdot^+/\text{A}\cdot^-$ ) and their subsequent recombination [18, 19]. Singlet excited molecules ( $^1\text{A}^*$  and  $^1\text{D}^*$ ) produced by recombination emit a quantum of light that is detected by experimental setup. The intensity of the detected luminescence is thus proportional to the probability of forming singlet excited molecules upon recombination. The effects of magnetic fields on recombination luminescence have as their origin spin evolution in geminate pairs and dependence of the yield of luminescence on the multiplicity of excited molecule formed by recombination.

An important advantage of non-polar solutions is that the initial inter-partner distance in the pairs after ionization (normally  $\sim 5\text{--}6$  nm) is substantially lower than Onsager radius ( $\sim 30$  nm for alkanes at room temperature). The overwhelming majority of the pairs thus recombine as geminate pairs, i.e., with their sibling counter ion. Upon ionization of molecule the spin of the ejected electron does not change its state. Since in the molecule the spins were paired, the initial spin state of the geminate pair is always singlet. Charge transfer to acceptors and charge recombination also do not change spin states. This means that the multiplicity of the excited molecule formed by recombination is determined by the multiplicity of the recombining pair immediately before recombination. The multiplicity of the excited molecule is thus determined by spin evolution of the geminate radical ion pair between the moments of ionization and recombination. Static or oscillating magnetic fields can substantially affect this evolution. And finally, as excited molecules normally emit light from their singlet excited state, any effect of magnetic fields on the spin state of the pair is directly reflected in the intensity of recombination luminescence.

In liquid non-polar solution the partners of the pair formed by irradiation spend almost the entire period of time from ionization and up to recombination at substantial distances from each other (tens of nanometres), as their approach to distances about 1–2 nm leads to practically instant recombination. Thus dipole–dipole and exchange interactions between the pair partners can be safely neglected. Spin evolution of the pair in this case is driven by interaction of electron spin with spins of nuclei (hyperfine interaction, HFI), with external magnetic fields, and by spin relaxation processes.

Spin Hamiltonian for the radical pair consisting of radicals  $A$  and  $D$  in high static magnetic field  $\mathbf{B}_0$  and microwave field with magnetic component  $\mathbf{B}_1(t)$  can be written as

$$\hat{H} = g\mu_B[\mathbf{B}_0 + \mathbf{B}_1(t)](\hat{\mathbf{S}}^A + \hat{\mathbf{S}}^D) + \hat{S}_z^A \sum_i a_i^A \hat{I}_{zi}^A + \hat{S}_z^D \sum_j a_j^D \hat{I}_{zj}^D, \quad (1)$$

where  $\hat{\mathbf{S}}^A$  and  $\hat{\mathbf{S}}^D$  are spin operators for electrons, and  $\hat{I}_i^A$  and  $\hat{I}_j^D$  are spin operators for magnetic nuclei in radicals  $A$  and  $D$  respectively. The sum runs over the nuclei of radicals. The first term describes Zeeman interaction of electron spins with external magnetic field, and the second and third terms correspond to isotropic hyperfine interaction of electron spins with nuclear spins in the two radicals. The  $z$  axis is aligned along the direction of the field  $\mathbf{B}_0$ . For simplicity we assume that the partners of the pair have identical  $g$ -values ( $g_A = g_D = g$ ).

As was shown in work [12] in the presence of spin relaxation time evolution of the spin operators for the partners of the radical pair  $\hat{\mathbf{S}}^A(t)$  and  $\hat{\mathbf{S}}^D(t)$  is described by a system of equations in the frame rotating at the frequency of the applied microwave field that are similar to Bloch equations [20, 21]. For operator  $\hat{\mathbf{S}}^A(t)$  the system is written as

$$d\hat{S}_x^A/dt = -\Delta\omega^A \hat{S}_y^A - \hat{S}_x^A/T_2^A, \quad (2a)$$

$$d\hat{S}_y^A/dt = \Delta\omega^A \hat{S}_x^A - \omega_1 \hat{S}_z^A - \hat{S}_y^A/T_2^A, \quad (2b)$$

$$d\hat{S}_z^A/dt = \omega_1 \hat{S}_y^A - \hat{S}_z^A/T_1^A, \quad (2c)$$

where  $\omega_1 = g\mu_B B_1/\hbar$ ,  $T_1^A$  and  $T_2^A$  are the times of spin–lattice and spin–spin relaxation. The  $z$  axis is aligned in the direction of the static magnetic field, and the  $x$  axis points along the  $B_1$  field.  $\Delta\omega^A = \omega^A - \omega_0$  is the detuning of the hyperfine component (HFC) of radical  $A$  from resonance. Here  $\omega_0$  is the frequency of the applied microwave field, and  $\omega^A = (g\mu_B B_0 + \sum a_i^A I_i^A)/\hbar$  is the resonance frequency for radical  $A$ . Time evolution for partner  $\hat{S}^D(t)$  is described by similar equations after substituting  $D$  for  $A$ . Equilibrium magnetization of spins in magnetic field was neglected in the system (2a)–(2c) to simplify the following calculations. This is a good approximation if the spin state of the pair is far from equilibrium during the entire observation time. This condition is always met for spin evolution of a radical ion pair from its singlet initial state at room temperature on the nanosecond time scale.

In the absence of interactions between the spins of the pair, the spin state of the pair can be described using operators of projection  $\hat{P}_\psi(t)$  on an arbitrary state  $|\psi\rangle$  written through  $\hat{S}^A(t)$  and  $\hat{S}^D(t)$ :

$$w_\psi(t) = \text{Tr}[\hat{P}_\psi(t)\hat{\rho}(0)], \quad (3)$$

where  $w_\psi(t)$  is the probability of finding the system in the state  $|\psi\rangle$ . Some  $\hat{P}_\psi(t)$  are given in appendix C.

## 2.2. Solution of the coupled operator equations

Coupled equations (2a)–(2c) are a system of homogeneous linear differential equations, and its solution can be represented as an expansion over a complete orthonormal basis. In our case such a basis is conveniently given by Pauli matrices  $\hat{\sigma}_x$ ,  $\hat{\sigma}_y$  and  $\hat{\sigma}_z$ .

$$\hat{S}_i^{A,D}(t) = \sum_k \Lambda_{ik}^{A,D}(t)\hat{S}_k(0), \quad i, k = x, y, z, \quad (4)$$

where  $\hat{S}_i(0) = \frac{1}{2}\hat{\sigma}_i$ ,  $i = x, y, z$ .

The system (2a)–(2c) was solved by Laplace transform and its inversion along the lines of the work [22]. Alternatively, the generalized coupled equations are solved numerically [23]. A substantial difference from [22] is that in our case the equations are solved for operators, but this does not change the basic approach.

Laplace transform of the original equations yields the following system:

$$(p + 1/T_2)\hat{\tilde{S}}_x + \Delta\omega\hat{\tilde{S}}_y = \hat{\tilde{S}}_x(0), \quad (5a)$$

$$-\Delta\omega\hat{\tilde{S}}_x + (p + 1/T_2)\hat{\tilde{S}}_y + \omega_1\hat{\tilde{S}}_z = \hat{\tilde{S}}_y(0), \quad (5b)$$

$$-\omega_1\hat{\tilde{S}}_y + (p + 1/T_1)\hat{\tilde{S}}_z = \hat{\tilde{S}}_z(0), \quad (5c)$$

where the tilde sign denotes Laplace transforms of the corresponding spin operators and  $p$  is the Laplace parameter. This system is a system of linear algebraic equations with three unknowns, which has a unique solution when its determinant is nonzero

$$\Delta(p) = (p + 1/T_2)^2(p + 1/T_1) + \Delta\omega^2(p + 1/T_1) + \omega_1^2(p + 1/T_2). \quad (6)$$

The solution of the system (5a)–(5c) has the following form:

$$\hat{\tilde{S}} = \frac{1}{\Delta(p)} \begin{pmatrix} (p + \frac{1}{T_2})(p + \frac{1}{T_1}) + \omega_1^2 & -(p + \frac{1}{T_1})\Delta\omega & \Delta\omega\omega_1 \\ (p + \frac{1}{T_1})\Delta\omega & (p + \frac{1}{T_1})(p + \frac{1}{T_2}) & -(p + \frac{1}{T_2})\omega_1 \\ \Delta\omega\omega_1 & (p + \frac{1}{T_2})\omega_1 & \Delta\omega^2 + (p + \frac{1}{T_2})^2 \end{pmatrix} \hat{\tilde{S}}(0). \quad (7)$$

To take inverse Laplace transform from expressions (7) we need to factorize the determinant  $\Delta(p)$ . The determinant is a cubic polynomial with respect to  $p$ , and its roots are given by Cardano formula. Depending on whether the discriminant of the equation

$$\xi = q^2/4 + s^3/27 \quad (8)$$

is positive, negative or zero (two cases of degeneration), four types of solution are possible. We introduced the following notation:

$$q = 2b^3/27 - bc/3 + d, \quad s = -b^2/3 + c, \quad b = 2/T_2 + 1/T_1, \quad (9)$$

$$c = 1/T_2^2 + 2/(T_1 T_2) + \Delta\omega^2 + \omega_1^2, \quad d = 1/(T_2^2 T_1) + \Delta\omega^2/T_1 + \omega_1^2/T_2. \quad (10)$$

As can be seen from equations (7), in all cases the following relations hold true:

$$\Lambda_{yx}(t) = -\Lambda_{xy}(t), \quad \Lambda_{zx}(t) = \Lambda_{xz}(t), \quad \Lambda_{zy}(t) = -\Lambda_{yz}(t). \quad (11)$$

*Case:  $\xi > 0$ .* In this case the polynomial  $\Delta(p)$  has one real and two complex conjugate roots (the roots of  $\Delta(p)$  are  $-p_1$  and  $-p_2 \pm ip_3$ ):  $\Delta(p) = (p + p_1)[(p + p_2)^2 + p_3^2]$ , where  $p_1 = b/3 - (y_+ + y_-)$ ,  $p_2 = b/3 + (y_+ + y_-)/2$ ,  $p_3 = \sqrt{3}(y_+ - y_-)/2$ ,  $y_{\pm} = (-q/2 \pm \sqrt{\xi})^{1/3}$ . This case corresponds to an oscillatory solution:

$$\Lambda_{ik}(t) = A_{ik} e^{-p_1 t} + B_{ik} e^{-p_2 t} \cos(p_3 t) + \frac{1}{p_3} C_{ik} e^{-p_2 t} \sin(p_3 t), \quad (12)$$

The coefficients were found by a procedure similar to the method used in the work [22]. The expressions for the coefficients are given in appendix A.

The solutions for species type *A* and type *D* are similar and differ only in the corresponding indices (*A* or *D*) for parameters  $\Delta\omega$ ,  $T_1$  and  $T_2$ .

Appendix A does not provide expressions for coefficients  $\Lambda_{yx}(t)$ ,  $\Lambda_{zx}(t)$  and  $\Lambda_{zy}(t)$ , as they can be easily obtained from formulae (11).

*Case: Negative discriminant ( $\xi < 0$ ).* In this case the polynomial  $\Delta(p)$  has three real roots:  $\Delta(p) = (p + p_1)(p + p_2)(p + p_3)$ , where  $p_1 = b/3 + 2\rho \cos(\phi/3)$ ,  $p_2 = b/3 - 2\rho \cos(\pi/3 - \phi/3)$ ,  $p_3 = b/3 - 2\rho \cos(\pi/3 + \phi/3)$ ,  $\rho = \pm\sqrt{-s/3}$ ,  $\cos(\phi) = q/(2\rho^3)$  and the sign of  $\rho$  must coincide with the sign of  $q$ . Similar to the first case we obtain

$$\Lambda_{ik}(t) = C_{ik}^1 e^{-p_1 t} (p_3 - p_2) + C_{ik}^2 e^{-p_2 t} (p_1 - p_3) + C_{ik}^3 e^{-p_3 t} (p_2 - p_1). \quad (13)$$

This case corresponds to a overdamped solution (all  $p_i > 0$ ).

The expressions for the coefficients  $C_{ik}^l$  are given in appendix A. Coefficients  $\Lambda_{yx}(t)$ ,  $\Lambda_{zx}(t)$  and  $\Lambda_{zy}(t)$  can be found using formulae (11).

*Case:  $\xi = 0$ .* In this case the determinant  $\Delta(p)$  has three real roots, two of which coincide:  $\Delta(p) = (p + p_1)(p + p_2)^2$ , where  $p_1 = b/3 - 2(-q/2)^{1/3}$ ,  $p_2 = b/3 + (-q/2)^{1/3}$ . In this case

$$\Lambda_{ik}(t) = A_{ik} e^{-p_1 t} + B_{ik} e^{-p_2 t} + C_{ik} t e^{-p_2 t}. \quad (14)$$

*Case:  $\xi = 0$  and  $q = 0$ .* In this case the determinant  $\Delta(p)$  has three coinciding real roots:  $\Delta(p) = (p + p_1)^3$ , where  $p_1 = b/3 = (2/T_2 + 1/T_1)/3$ . In this case

$$\Lambda_{ik}(t) = A_{ik} e^{-p_1 t} + B_{ik} t e^{-p_1 t} + C_{ik} \frac{t^2}{2} e^{-p_1 t}. \quad (15)$$

This case (double degeneration) occurs when  $\omega_1 = 2\sqrt{2}\Delta\omega$  and  $(1/T_2 - 1/T_1) = 3\sqrt{3}\Delta\omega$ .

The degenerate cases (14) and (15) never occur in actual calculations, so we do not provide expressions for their coefficients.

### 3. Some peculiarities of spin dynamics

A convenient basis for spin states of the radical pair is given by Bell functions:

$$|S\rangle = |\psi^-\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle), \quad (16a)$$

$$|T_x\rangle = |\phi^-\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle - |\downarrow\rangle|\downarrow\rangle), \quad (16b)$$

$$|T_y\rangle = |\phi^+\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle + |\downarrow\rangle|\downarrow\rangle), \quad (16c)$$

$$|T_z\rangle = |\psi^+\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle), \quad (16d)$$

where  $|\uparrow\rangle$  and  $|\downarrow\rangle$  are eigenstates of radical with spin projection on the  $z$  axis equal to  $+1/2$  and  $-1/2$  respectively. In the product the left function always corresponds to radical  $A$  and the right function to radical  $D$ . The singlet function  $|S\rangle$  has zero total spin, and the three triplet functions  $|T_x\rangle$ ,  $|T_y\rangle$  and  $|T_z\rangle$  have total spin equal to 1 and zero projection on axes  $x$ ,  $y$  and  $z$  respectively.

Specialists in spin chemistry are more used to working in the basis of the singlet function  $|S\rangle$  and the three triplet functions  $|T_0\rangle$ ,  $|T_+\rangle$  and  $|T_-\rangle$  with defined projection of the total spin on the  $z$  axis equal to 0,  $+1$  and  $-1$  respectively (it is this notation that was used in figure 1). As equations (16b)–(16d) show, the Bell functions are expressed from them as follows:

$$|T_z\rangle = |T_0\rangle, \quad |T_x\rangle = \frac{1}{\sqrt{2}}(|T_+\rangle - |T_-\rangle), \quad |T_y\rangle = \frac{1}{\sqrt{2}}(|T_+\rangle + |T_-\rangle).$$

The expressions for spin projection operators  $\hat{P}_{ij}$  in the basis  $|S\rangle$ ,  $|T_x\rangle$ ,  $|T_y\rangle$ ,  $|T_z\rangle$  are given in appendix C.

Let us introduce notation for the density matrix written in this basis at time zero:

$$\hat{\rho}(0) = \begin{pmatrix} \rho_{ss} & \rho_{sx} & \rho_{sy} & \rho_{sz} \\ \rho_{xs} & \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{ys} & \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zs} & \rho_{zx} & \rho_{zy} & \rho_{zz} \end{pmatrix}. \quad (17)$$

In our calculations we shall also use a particular case when the initial state of the pair at zero time is given by a wavefunction that is a linear combination of singlet  $|S\rangle$  and triplet  $|T_z\rangle$  states:

$$|\Psi\rangle(0) = \cos\theta|S\rangle + \sin\theta e^{i\phi}|T_z\rangle. \quad (18)$$

In this case  $\rho_{ss} = \cos^2\theta$ ,  $\rho_{zz} = \sin^2\theta$ ,  $\rho_{sz} = \frac{1}{2}\sin 2\theta e^{-i\phi}$ ,  $\rho_{zs} = \frac{1}{2}\sin 2\theta e^{i\phi}$ , all other  $\rho_{ij}$  are equal to zero.

#### 3.1. Spin dynamics in the absence of spin relaxation

In the absence of spin relaxation, i.e. for  $1/T_1 = 1/T_2 = 0$ , the calculations become substantially simpler, which allows us to get a number of important results analytically. In this an oscillatory solution always occurs:

$$\Lambda_{ik}(t) = A_{ik} + B_{ik} \cos(\omega t) + \frac{1}{\omega} C_{ik} \sin(\omega t), \quad (19)$$

where  $\omega = \sqrt{\omega_1^2 + \Delta\omega^2}$ .

3.1.1. *Spin dynamics in the absence of microwave pumping* ( $\omega_1 = 0$ ). As it follows from expressions (C.1)–(C.4),

$$\hat{P}_{ss} + \hat{P}_{zz} = |S\rangle\langle S| + |T_z\rangle\langle T_z| = \frac{1}{2} - 2\hat{S}_z^A(t)\hat{S}_z^D(t), \quad (20)$$

$$\hat{P}_{xx} + \hat{P}_{yy} = |T_x\rangle\langle T_x| + |T_y\rangle\langle T_y| = \frac{1}{2} + 2\hat{S}_z^A(t)\hat{S}_z^D(t). \quad (21)$$

For each radical we can write

$$\hat{S}_z(t) = \frac{\Delta\omega\omega_1}{\omega^2} (1 - \cos(\omega t)) \hat{S}_x(0) + \frac{\omega_1}{\omega} \sin(\omega t) \hat{S}_y(0) + \left( \frac{\Delta\omega^2}{\omega^2} + \frac{\omega_1^2}{\omega^2} \cos(\omega t) \right) \hat{S}_z(0). \quad (22)$$

For  $\omega_1 = 0$  and considering (C.5)–(C.13) we have

$$\text{Tr}[\hat{S}_z^A(t)\hat{S}_z^D(t)\rho(0)] = \frac{1}{4}(-\rho_{ss} + \rho_{xx} + \rho_{yy} - \rho_{zz}), \quad (23)$$

where we used the notation of (17).

From (20), (23) and from the normalization condition

$$\rho_{ss} + \rho_{xx} + \rho_{yy} + \rho_{zz} = 1 \quad (24)$$

it follows that for  $\omega_1 = 0$  the sum of populations of the singlet  $|S\rangle$  state  $\rho_{ss}(t)$  and the triplet  $|T_z\rangle$  state  $\rho_{zz}(t)$  does not depend on time:

$$\rho_{ss}(t) + \rho_{zz}(t) = \rho_{ss} + \rho_{zz}. \quad (25)$$

This is a quite natural result, since in the absence of microwave pumping and spin relaxation the only possible transitions in the system are between the states  $|S\rangle$  and  $|T_z\rangle$  due to hyperfine interaction or differences in the  $g$ -values of the pair partners. The two other triplet states  $|T_+\rangle$  and  $|T_-\rangle$  (that can be linearly combined to produce the  $|T_x\rangle$  and  $|T_y\rangle$  states) under these conditions are stationary, and their population does not change in time due to substantial Zeeman splitting.

3.1.2. *Spin dynamics in a strong microwave field* ( $\Delta\omega/\omega_1 \rightarrow 0$ ). As it follows from expressions (C.1)–(C.4),

$$\hat{P}_{ss} + \hat{P}_{xx} = |S\rangle\langle S| + |T_x\rangle\langle T_x| = \frac{1}{2} - 2\hat{S}_x^A(t)\hat{S}_x^D(t), \quad (26)$$

$$\hat{P}_{yy} + \hat{P}_{zz} = |T_y\rangle\langle T_y| + |T_z\rangle\langle T_z| = \frac{1}{2} + 2\hat{S}_x^A(t)\hat{S}_x^D(t). \quad (27)$$

Since for each radical

$$\hat{S}_x(t) = \left( \frac{\omega_1^2}{\omega^2} + \frac{\Delta\omega^2}{\omega^2} \cos(\omega t) \right) \hat{S}_x(0) - \frac{\Delta\omega}{\omega} \sin(\omega t) \hat{S}_y(0) + \frac{\Delta\omega\omega_1}{\omega^2} (1 - \cos(\omega t)) \hat{S}_z(0), \quad (28)$$

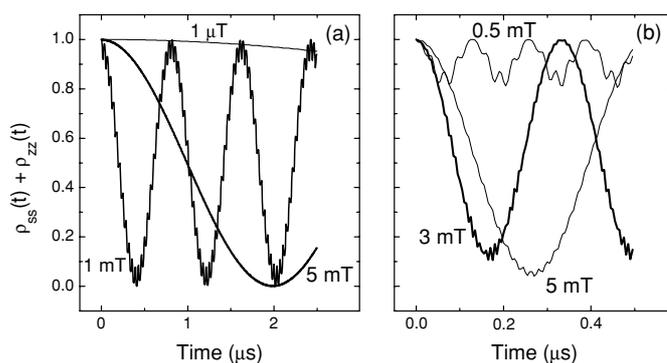
for  $\Delta\omega/\omega_1 \rightarrow 0$  considering (C.5)–(C.13) we have

$$\text{Tr}[\hat{S}_x^A(t)\hat{S}_x^D(t)\rho(0)] \rightarrow \frac{1}{4}(-\rho_{ss} - \rho_{xx} + \rho_{yy} + \rho_{zz}). \quad (29)$$

From (26), (29) and (24) we obtain that in the limit of the strong microwave field a new invariant appears. The sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states does not depend on time:

$$\rho_{ss}(t) + \rho_{xx}(t) \approx \rho_{ss} + \rho_{xx}. \quad (30)$$

The smaller the ratio  $\Delta\omega/\omega_1$ , the more accurate the equality.



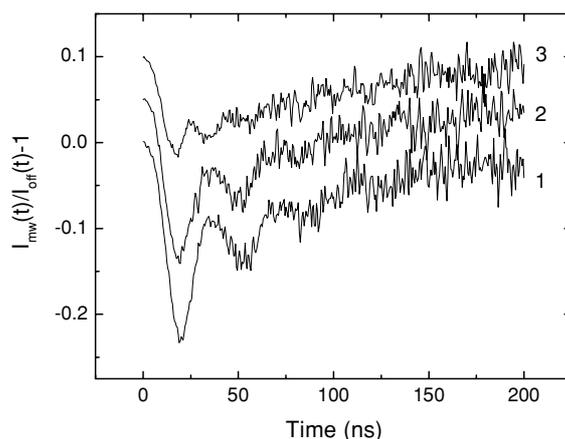
**Figure 2.** Time dependence of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_z\rangle$  states.  $\Delta B_A = 0$ ,  $\Delta B_D = 0.3$  mT (a);  $\Delta B_A = 1$  mT,  $\Delta B_D = 1.3$  mT (b). The value of  $B_1$  is indicated next to its corresponding curve.

**3.1.3. Spin dynamics in microwave fields of finite strength.** The situation in arbitrary microwave fields is more complex than in the limiting cases discussed above, so we shall consider the general properties of the obtained solutions using several specific examples as an aid.

Figure 2(a) shows time dependences of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_z\rangle$  states of the system at different magnitudes of  $B_1$ . The line of one radical is precisely in resonance with the applied microwave field, and the line of the other partner is detuned by 0.3 mT. The initial state of the pair was taken to be singlet, i.e.  $\rho_{ss} = 1$ , all other  $\rho_{ij} = 0$ . For figure 2 and all following figures  $\Delta B_{A,D} = \hbar \Delta \omega^{A,D} / (g \mu_B)$  is taken. As the figure shows, in this case even a weak microwave field is sufficient to completely destroy invariant (25). The reason for this is transitions between  $|T_z\rangle$  and  $|T_y\rangle$  states induced by the resonant microwave field. As a consequence the value of  $\rho_{ss}(t) + \rho_{zz}(t)$  periodically changes from zero to one. The population of the singlet state also changes periodically (see figure 7). This phenomenon is referred to as quantum oscillations and has been observed experimentally [10–12] and studied theoretically [12, 13]. The changes in the frequency of oscillations with increasing amplitude of the microwave field are not monotonous. The frequency first increases but then, as  $B_1$  grows substantially larger than the splitting between the lines of the two radicals, falls down. The decrease of the frequency is related to the effect of spin locking.

Figure 2(b) shows time dependences  $\rho_{ss}(t) + \rho_{zz}(t)$  in the situation of strong detuning of the microwave frequency from resonance. Time scale is expanded five times with respect to figure 2(a). As is clear from the figure, in this case for not too large amplitudes of the microwave field the frequency of oscillations substantially increases as compared to the case of resonance with accompanying decrease in the amplitude of the oscillations.

This effect can be observed experimentally. Figure 3 shows experimental results on monitoring kinetics of recombination fluorescence from liquid alkane solutions in the absence and in the presence of the microwave field. The experimental technique that was used to get the presented traces was described in detail in work [12]. The processes initiated in the sample under the action of a short pulse of x-irradiation are given in subsection 2.1. Dodecane was used as the solvent (RH), hexafluorobenzene  $C_6F_6$  served as the electron acceptor (A) and deuterated *para*-terphenyl PTP- $d_{14}$  as the hole acceptor (D). ESR spectrum of PTP- $d_{14}$  radical cation is a single inhomogeneously broadened line with width about 0.1 mT. Radical anion of  $C_6F_6$  has a wide resolved spectrum with hyperfine coupling constant of about 13.5 mT with six equivalent fluorine nuclei [24]. Time dependence of the intensity of recombination



**Figure 3.** Experimentally observed microwave field effect in the kinetics of recombination fluorescence from a dodecane solution of  $10^{-4}$  M PTP- $d_{14}$  and  $10^{-2}$  M  $C_6F_6$  under the conditions of resonance (1) and with detuning of 0.3 mT (2) and 1.3 mT (3).  $B_1 = 1$  mT. For convenience the curves 2 and 3 are shifted upwards by 0.05 and 0.1 respectively.

fluorescence  $I(t)$  was sampled using the single photon counting technique. The observed light in this case mostly comes from excited PTP- $d_{14}$  molecules. Since recombination kinetics  $f(t)$  does not depend on the multiplicity of the pair, and fluorescence intensity is proportional to the singlet state population of the pair at the moment of recombination  $\rho_{ss}(t)$ , we can write that  $I(t) \approx f(t)\rho_{ss}(t)$ . The equality becomes more accurate as fluorescence time of the luminophore shortens (about 1 ns for PTP- $d_{14}$ ) and time resolution of the experimental setup improves (about 3 ns in our case). Under these conditions time resolved microwave field effect is given by

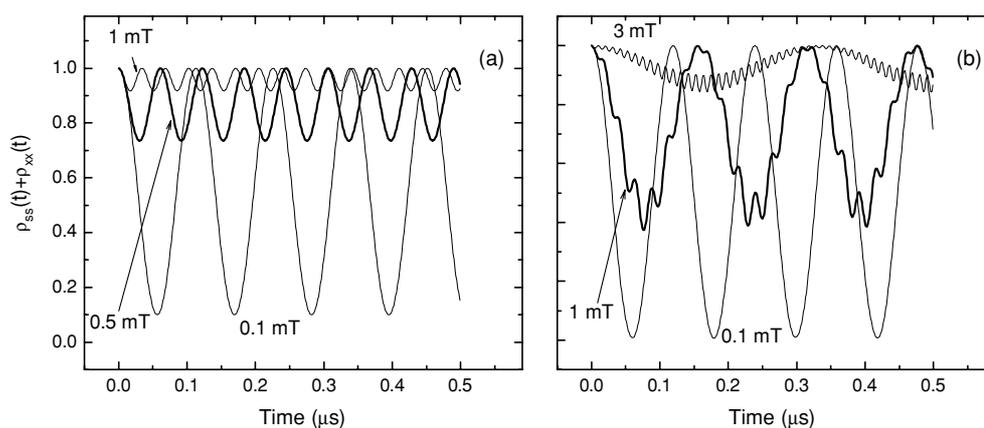
$$I_{mw}(t)/I_{off}(t) - 1 \approx \rho_{ss}^{mw}(t)/\rho_{ss}^{off}(t) - 1, \quad (31)$$

where  $I_{mw}(t)$  and  $\rho_{ss}^{mw}(t)$  are luminescence kinetics and time dependence of the singlet state population in the presence of the microwave field, and  $I_{off}(t)$  and  $\rho_{ss}^{off}(t)$  are the same functions in the absence of the field.

Figure 3 shows three curves. Curve 1 corresponds to conditions of microwave field resonance for radical cation of PTP- $d_{14}$ , curves 2 and 3 to detuning from resonance by 0.3 mT and 1.3 mT respectively. As can be seen from the figure, the experimental curves are modulated with oscillations. The frequency of oscillations increases with increase in the detuning, and their amplitude falls down in qualitative agreement with the results of theoretical calculations shown in figure 2. Because of rather large HFI constants in radical anion of  $C_6F_6$  the populations of  $|S\rangle$  and  $|T_z\rangle$  states can be considered equal at any time, and  $\rho_{ss}(t) = \frac{1}{2}[\rho_{ss}(t) + \rho_{zz}(t)]$ . Experimental curves are noisy as they were not passed through any smoothing routines, and the figure shows that noise level increases with time. As was shown in work [12], it is proportional to  $t^{3/4}$ .

As figure 2(b) shows for large magnitudes of  $B_1$  in the case of detuning from resonance the frequency of oscillations also decreases, but this happens at larger amplitudes of the microwave field than under the conditions of resonance and is accompanied with increasing amplitude of the oscillations.

Figure 4(a) shows time dependences of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states at several amplitudes of the microwave field. In the calculations it was assumed that one radical is precisely in resonance with the applied microwave field, and the



**Figure 4.** Time dependence of the sum of populations of the singlet  $|S\rangle$  and triplet  $|T_x\rangle$  states for different amplitudes of the microwave field. The magnitude of  $B_1$  is indicated next to its corresponding curve.  $\Delta B_A = 0$ ,  $\Delta B_D = 0.3$  mT (a);  $\Delta B_A = 1$  mT,  $\Delta B_D = 1.3$  mT (b).

line of the second radical is detuned by 0.3 mT. All calculations were performed for the singlet initial state. Figure 4(b) shows the results of calculations similar to those shown in figure 4(a), but with detuning from resonance by 1 mT.

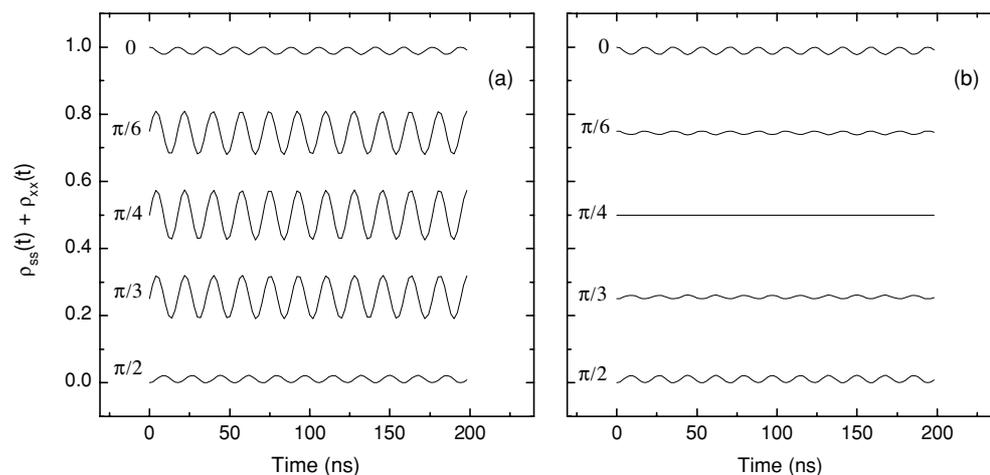
As figure 4 shows, the behaviour of these curves qualitatively differs from the curves of figure 2. An increase in the amplitude of the microwave field leads to increased frequency and decreased amplitude of the oscillations. Such a behaviour of the calculated curves reflects the existence of the high field invariant (30). It can be noted that the accuracy of conserving the value of  $\rho_{ss}(t) + \rho_{xx}(t)$  at small splitting is rather high already for microwave field amplitudes easily accessible in experiment. The magnitudes of  $B_1$  amplitudes required for conserving the high field invariant increase in the case of detuning from resonance (or increasing the value of  $\Delta\omega$ ).

For the singlet initial state of the pair and sufficiently large magnitude of  $B_1$  the sum of populations  $\rho_{ss}(t) + \rho_{xx}(t)$  oscillate close to 1, as can be seen from figure 4, which is in good agreement with equation (30). In a more general case (18), when the initial singlet state population  $\rho_{ss}(0)$  is equal to  $\cos^2\theta$ , the sum of populations  $\rho_{ss}(t) + \rho_{xx}(t)$  should oscillate close to this value  $\cos^2\theta$ . The correctness of this conclusion is demonstrated by the results of calculations given in figure 5, which shows time dependences of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states of the system for different initial conditions (18). The curves that are shown in this figure correspond to several sets of values of  $\theta$  and  $\phi$ . As can be clearly seen, the curves in fact oscillate close to the level of  $\cos^2\theta$ . The frequency of these oscillations is indeed close to  $\omega_1$ , and their amplitude depends on  $\phi$ .

### 3.2. On the possibility of controlling the spin state of the radical ion pair

The existence of invariants (25) and (30) significantly simplifies the analysis of spin evolution of radical ion pairs in the absence of the microwave field and in strong microwave fields. This opens important possibilities for controlled impact on the pair to manipulate its spin state.

As was demonstrated in [15], the existence of the high field invariant (30) allows us, in principle, to perform ‘true spin locking’. Upon rapid application of a strong microwave field at the moment when the pair is in its triplet  $|T_z\rangle$  state the system is ‘locked’ in the triplet state



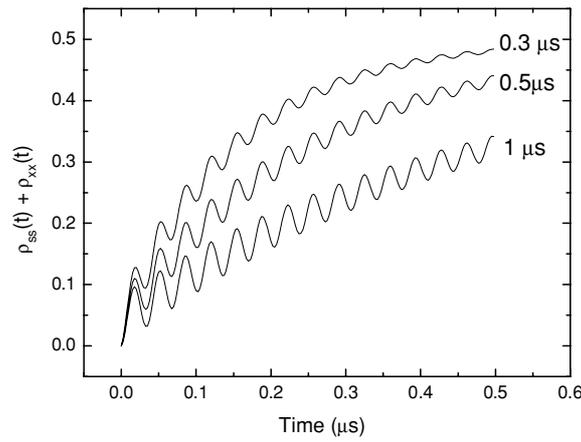
**Figure 5.** Time dependence of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states for different initial conditions given by equation (18). The values of  $\theta$  are indicated next to their corresponding curves.  $\phi = \pi/2$  (a) and 0 (b).  $\Delta B_A = 0$ ,  $\Delta B_D = 0.3$  mT.  $B_1 = 2$  mT.

and cannot get into the singlet state. At the same time for the singlet initial state the system cannot be completely ‘locked’, and the singlet state population oscillates at a frequency close to  $\Delta\omega_{AD}^2/2\omega_1$ , where  $\Delta\omega_{AD} = \omega^A - \omega^D$ , where  $\omega^A$  and  $\omega^D$  are resonance frequencies for radicals  $A$  and  $D$  respectively [13]. This effect is made absolutely clear by the existence of the high field invariant (30). For the singlet initial state the sum of populations  $\rho_{ss}(t) + \rho_{xx}(t)$  is equal to 1 all the time, and the populations  $\rho_{ss}(t)$  and  $\rho_{xx}(t)$  change in antiphase with frequency  $\Delta\omega_{AD}^2/2\omega_1$ . The population of the state  $|T_z\rangle$  always remains very close to zero [13, 15]. From the invariant (30) it follows that the population of the state  $|T_y\rangle$  also remains zero. For triplet initial state  $|T_z\rangle$  the sum of populations  $\rho_{ss}(t)$  and  $\rho_{xx}(t)$  remains zero all the time, which means that populations  $\rho_{ss}(t)$  and  $\rho_{xx}(t)$  remain zero.

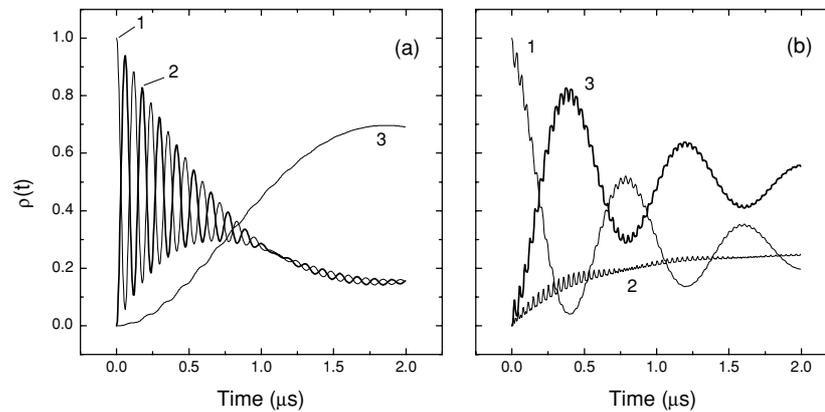
In radiation processes the initial state of the pair is always singlet. However the pair can be transferred into the triplet state  $|T_z\rangle$  due to the existence of invariant (25). In the absence of the microwave field only the states  $|S\rangle$  and  $|T_z\rangle$  get populated. If the frequencies of transitions between them  $\Delta\omega_{AD}$  for different pairs in the sample are multiples of each other, as it happens when there is an odd number of equivalent magnetic nuclei in the radical ion, there are moments when all pairs are in their  $|T_z\rangle$  states. If a strong microwave field is applied at this time, the effect of ‘true spin locking’ can be observed.

### 3.3. The effect of relaxation

The above considerations are valid only in the absence of spin relaxation, which destroys spin invariants. The zero microwave field invariant (25) is apparently destroyed by spin-lattice relaxation. Phase relaxation does not affect this invariant. This means that expression (25) holds true only for times substantially smaller than  $T_1$ . The effect of relaxation on the high field invariant (30) is much less obvious. Figure 6 shows transformations of time dependence for the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states of the pair with changing phase relaxation time  $T_2$ . In the absence of relaxation because of invariant (30) the total population of  $\rho_{ss}(t)$  and  $\rho_{xx}(t)$  should oscillate close to zero. However the figure shows that this is no longer the case. The total population increases with time, and the time scale of this



**Figure 6.** Time dependence of the sum of populations of the singlet  $|S\rangle$  and the triplet  $|T_x\rangle$  states. Initial state is  $|T_z\rangle$ .  $B_1 = 1$  mT,  $T_1^A = T_1^D = 10$   $\mu$ s,  $\Delta B_A = 0$ ,  $\Delta B_D = 0.3$  mT,  $T_2^A = T_2^D = T_2$ . Numerical values of  $T_2$  are indicated next to the corresponding curves.



**Figure 7.** Time dependence of the populations of the singlet state  $|S\rangle$  (1), triplet state  $|T_z\rangle$  (2) and the sum of populations of the triplet states  $|T_x\rangle$  and  $|T_y\rangle$  (3) for  $T_1^A = T_1^D = 1$  s,  $T_2^A = T_2^D = 1$   $\mu$ s.  $\Delta B_A = 0$ ,  $\Delta B_D = 0.3$  mT.  $B_1 = 10$   $\mu$ T (a) and 1 mT (b).

increase is close to the phase relaxation time  $T_2$ . We conclude it is phase relaxation that causes the destruction of the high field invariant (30).

Figure 7 shows time dependences of the populations of different states in the cases of weak and strong microwave fields in the presence of phase relaxation.

The time of spin-lattice relaxation  $T_1$  in this model calculation is taken to be very large, so it has practically no effect on the obtained curves.

As figure 7 shows, the time profile of the populations of different states is qualitatively different upon application of weak and strong microwave fields. In a weak field  $\rho_{ss}(t)$  and  $\rho_{zz}(t)$  oscillate in antiphase with frequency close to  $\Delta\omega_{AD}$ . The amplitude of these oscillations drops because of phase relaxation, and  $\rho_{ss}(t)$  and  $\rho_{zz}(t)$  asymptotically approach each other. The sum of populations  $\rho_{xx}(t) + \rho_{yy}(t)$  in this case is a more smooth curve, which is periodically modulated with frequency close to  $\omega_1$ .

In a strong microwave field we see the manifestations of spin locking. The singlet state population  $\rho_{ss}(t)$  oscillates at a frequency about  $\Delta\omega$  similar to the weak field case, but the amplitude of these oscillations is rather small. Oscillations of substantial amplitude occur at a frequency about  $\Delta\omega_{AD}^2/2\omega_1$ . This is also the frequency at which the sum of populations  $\rho_{xx}(t) + \rho_{yy}(t)$  changes. The population of the triplet state  $|T_z\rangle$  increases with the time of phase relaxation  $T_2$ .

#### 4. Conclusions

First of all we note that all these results were obtained in the case of fixed nuclear configurations in both partners of the pair. In the presence of the reaction of ion-molecular charge transfer this condition is no longer observed, but this apparently does not change the zero microwave field invariant (25). The high microwave field invariant (30) will also remain valid if the condition  $\Delta\omega/\omega_1 \ll 1$  is not violated in the course of the reaction.

Let us formulate the main rules for spin evolution of a radical pair that follow from the existence of invariants (25) and (30).

- (i) In the absence of microwave pumping the sum of populations of the states  $|S\rangle$  and  $|T_z\rangle$  (or  $|S\rangle$  and  $|T_0\rangle$  in different notation) remains constant at times shorter than  $T_1$ . The populations of these states oscillate at a frequency  $\omega^A - \omega^D$ , where  $\omega^A$  and  $\omega^D$  are resonance frequencies for radicals  $A$  and  $D$  respectively. It also naturally follows that the sum of populations of the states  $|T_x\rangle$  and  $|T_y\rangle$  (or  $|T_+\rangle$  and  $|T_-\rangle$ ) does not change as well. Invariant (25) is destroyed by spin-lattice relaxation. Even the weak resonant microwave field also destroys invariant (25). The sum of populations  $\rho_{ss}(t) + \rho_{zz}(t)$  starts oscillating at a frequency close to  $\omega_1$  (quantum oscillations induced by microwave field).
- (ii) In a strong resonant microwave field the sum of populations of the states  $|S\rangle$  and  $|T_x\rangle$ , as well as  $|T_y\rangle$  and  $|T_z\rangle$ , remains constant. The consequence of this is the effect of spin locking. The high field invariant (30) is rather accurately conserved already for not very large magnitudes of  $B_1$  quite accessible in experiment. The magnitude of  $B_1$  required to maintain invariant (30) increases with detuning from resonance. The high field invariant (30) is destroyed by phase relaxation.

The two invariants that we found suggest a way of controlling transitions between spin states of a radical pair. One possible variant of controlling the quantum spin state would be a rapid switching of a strong microwave field on and off. In this case the pair will alternatively be in the conditions when one of the invariants is conserved. Another possible control option may be a rapid change in the phase of the microwave field by  $\pi/2$ . In this case the axes  $x$  and  $y$  are exchanged, which correspondingly changes the populations of the  $|T_x\rangle$  and  $|T_y\rangle$  states.

#### Acknowledgments

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#### Appendix A. Coefficients in the expressions for different types of solutions of equations for spin dynamics

Case  $\xi > 0$  (for oscillatory solution)

$$\begin{aligned} A_{xx} &= (\alpha\beta + \omega_1^2)/\gamma, & A_{yy} &= \alpha\beta/\gamma, & A_{zz} &= (\beta^2 + \Delta\omega^2)/\gamma, \\ A_{xy} &= -\alpha\Delta\omega/\gamma, & A_{xz} &= \omega_1\Delta\omega/\gamma, & A_{yz} &= -\omega_1\beta/\gamma, \end{aligned}$$

$$\begin{aligned}
B_{xx} &= 1 - A_{xx}, & B_{yy} &= 1 - A_{yy}, & B_{zz} &= 1 - A_{zz}; \\
B_{xy} &= -A_{xy}, & B_{xz} &= -A_{xz}, & B_{yz} &= -A_{yz}; \\
C_{xx} &= (\alpha\beta + \omega_1^2)(p_1 - p_2)/\gamma + (\alpha + \beta + p_1 - p_2), \\
C_{yy} &= \alpha\beta(p_1 - p_2)/\gamma + (\alpha + \beta + p_1 - p_2), \\
C_{zz} &= (\beta^2 + \Delta\omega^2)(p_1 - p_2)/\gamma + (2\beta + p_1 - p_2), \\
C_{xy} &= -\Delta\omega[\alpha(p_1 - p_2) + \gamma]/\gamma, & C_{xz} &= \omega_1\Delta\omega(p_1 - p_2)/\gamma, \\
C_{yz} &= -\omega_1(\gamma + \beta(p_1 - p_2))/\gamma,
\end{aligned}$$

where

$$\alpha = 1/T_1 - p_1, \quad \beta = 1/T_2 - p_1, \quad \gamma = (p_2 - p_1)^2 + p_3^2.$$

Case  $\xi < 0$  (for overdamped solution)

$$\begin{aligned}
C_{xx}^l &= \frac{1}{\eta} \left\{ p_l^2 - \left( \frac{1}{T_1} + \frac{1}{T_2} \right) p_l + \omega_1^2 + \frac{1}{T_1 T_2} \right\}, \\
C_{yy}^l &= \frac{1}{\eta} \left\{ p_l^2 - \left( \frac{1}{T_1} + \frac{1}{T_2} \right) p_l + \frac{1}{T_1 T_2} \right\}, \\
C_{zz}^l &= \frac{1}{\eta} \left\{ p_l^2 - \frac{2}{T_2} p_l + \Delta\omega^2 + \frac{1}{T_2^2} \right\}, \\
C_{xy}^l &= \frac{\Delta\omega}{\eta} \left( p_l - \frac{1}{T_1} \right), & C_{xz}^l &= \frac{1}{\eta} \Delta\omega\omega_1, & C_{yz}^l &= \frac{\omega_1}{\eta} \left( p_l - \frac{1}{T_2} \right),
\end{aligned}$$

where  $l = 1, 2, 3$ ,  $\eta = (p_1 - p_2)(p_2 - p_3)(p_3 - p_1)$ .

## Appendix B. The values of parameters that lead to certain types of solution for equations of spin dynamics

To analyse the different cases of spin dynamics it would be very useful to have simple rules for determining the type of solution for the equations with the given set of parameters. As it turned out, these rules can be easily formulated, which will be done in this section.

As has been shown earlier, the exact analytical solution for the equations of spin dynamics can belong to one of the four types: oscillatory, overdamped and two degenerate, depending in the first place on the value of  $\xi$ .

To simplify further treatment let us introduce the new parameter:

$$z = 1/T_2 - 1/T_1.$$

Since  $T_2 \leq T_1$  in all cases,  $z \geq 0$ .

It turns out that relaxation times  $T_1$  and  $T_2$  enter the expressions for  $q$ ,  $s$  and  $\xi$  (8)–(10) only as the  $z$  parameter:

$$\begin{aligned}
q &= \frac{1}{3}(\omega_1^2 - \Delta\omega^2)z - \frac{2}{27}z^3, & s &= -\frac{1}{3}z^2 + \Delta\omega^2 + \omega_1^2, \\
\xi &= \frac{1}{108} [4\Delta\omega^2 z^4 + (8\Delta\omega^4 - 20\Delta\omega^2\omega_1^2 - \omega_1^4)z^2 + 4(\Delta\omega^2 + \omega_1^2)^3].
\end{aligned} \tag{B.1}$$

This means that the type of the sought solution depends only on the differences in the rates of spin–spin and spin–lattice relaxation, but not on the absolute values of the two rates.

As can be seen from expression (B.1),  $\xi$  is a quadratic function with respect to  $z^2$ , with branches of the parabola going upwards. This means that in the absence of real roots  $\xi$  is positive for all values of  $z$ . If the roots exist  $\xi$  is negative for values of  $z^2$  in-between the roots and is positive for  $z^2$  outside this range.

From  $\xi = 0$  it follows:

$$z_{1,2}^2 = \frac{1}{8\Delta\omega^2} (\omega_1^4 + 20\Delta\omega^2\omega_1^2 - 8\Delta\omega^4 \pm \sqrt{\omega_1^2(\omega_1^2 - 8\Delta\omega^2)^3}). \quad (\text{B.2})$$

The solutions exist for  $\omega_1 \geq 2\sqrt{2}\Delta\omega$ . It can be easily shown that both roots are positive.

From this we conclude that  $\xi > 0$  either for  $\omega_1 < 2\sqrt{2}\Delta\omega$ , or for  $\omega_1 > 2\sqrt{2}\Delta\omega$  when  $z < z_2$  or  $z > z_1$  ( $z_1$  corresponds to choice of ‘+’ in (B.2), and  $z_2$  to the choice of ‘-’ respectively). In this case we obtain a solution of the oscillatory type.

$\xi < 0$  for  $\omega_1 > 2\sqrt{2}\Delta\omega$  in the range  $z_2 < z < z_1$ . This set of parameters produces a solution of the overdamped type.

For  $\xi = 0$ , when either  $z = z_1$  or  $z = z_2$  we have a solution of the degenerate type.

Finally, when simultaneously  $\xi = 0$  and  $q = 0$  the case of double degeneracy takes place. It can be easily shown that this occurs for  $\omega_1 = 2\sqrt{2}\Delta\omega$  and  $z = 3\sqrt{3}\Delta\omega$ .

Especially interesting is the behaviour of the solution in the vicinity of resonance for one of the radical ions, that is, when  $\Delta\omega/\omega_1 \rightarrow 0$ . Small parameter expansion of (B.2) then yields

$$z_1 \approx \omega_1^2 / (2\Delta\omega) \rightarrow \infty, \quad z_2 \approx 2\omega_1.$$

Thus close to the resonance line an oscillatory solution will be obtained for  $\omega_1 > \frac{1}{2}(1/T_2 - 1/T_1)$ , and an overdamped solution for  $\omega_1 < \frac{1}{2}(1/T_2 - 1/T_1)$ .

### Appendix C. Spin operators

Below we express projection operators of the basis states in the representation  $|S\rangle, |T_x\rangle, |T_y\rangle, |T_z\rangle$  in terms of spin operators of the pair partners:

$$\hat{P}_{ss} = |S\rangle\langle S| = \frac{1}{4} - \hat{S}_x^A \hat{S}_x^D - \hat{S}_y^A \hat{S}_y^D - \hat{S}_z^A \hat{S}_z^D, \quad (\text{C.1})$$

$$\hat{P}_{xx} = |T_x\rangle\langle T_x| = \frac{1}{4} - \hat{S}_x^A \hat{S}_x^D + \hat{S}_y^A \hat{S}_y^D + \hat{S}_z^A \hat{S}_z^D, \quad (\text{C.2})$$

$$\hat{P}_{yy} = |T_y\rangle\langle T_y| = \frac{1}{4} + \hat{S}_x^A \hat{S}_x^D - \hat{S}_y^A \hat{S}_y^D + \hat{S}_z^A \hat{S}_z^D, \quad (\text{C.3})$$

$$\hat{P}_{zz} = |T_z\rangle\langle T_z| = \frac{1}{4} + \hat{S}_x^A \hat{S}_x^D + \hat{S}_y^A \hat{S}_y^D - \hat{S}_z^A \hat{S}_z^D. \quad (\text{C.4})$$

Let us express the trace of the product of spin operators by the initial density matrix in the notation of (17):

$$\text{Tr}[\hat{S}_x^A(0)\hat{S}_x^D(0)\hat{\rho}(0)] = \frac{1}{4}(-\rho_{ss} - \rho_{xx} + \rho_{yy} + \rho_{zz}), \quad (\text{C.5})$$

$$\text{Tr}[\hat{S}_y^A(0)\hat{S}_y^D(0)\hat{\rho}(0)] = \frac{1}{4}(-\rho_{ss} + \rho_{xx} - \rho_{yy} + \rho_{zz}), \quad (\text{C.6})$$

$$\text{Tr}[\hat{S}_z^A(0)\hat{S}_z^D(0)\hat{\rho}(0)] = \frac{1}{4}(-\rho_{ss} + \rho_{xx} + \rho_{yy} - \rho_{zz}), \quad (\text{C.7})$$

$$\text{Tr}[\hat{S}_x^A(0)\hat{S}_y^D(0)\hat{\rho}(0)] = \frac{i}{4}(\rho_{zs} - \rho_{yx} + \rho_{xy} - \rho_{sz}), \quad (\text{C.8})$$

$$\text{Tr}[\hat{S}_x^A(0)\hat{S}_z^D(0)\hat{\rho}(0)] = \frac{1}{4}(-\rho_{ys} + \rho_{zx} - \rho_{sy} + \rho_{xz}), \quad (\text{C.9})$$

$$\text{Tr}[\hat{S}_y^A(0)\hat{S}_x^D(0)\hat{\rho}(0)] = \frac{i}{4}(-\rho_{zs} - \rho_{yx} + \rho_{xy} + \rho_{sz}), \quad (\text{C.10})$$

$$\text{Tr}[\hat{S}_y^A(0)\hat{S}_z^D(0)\hat{\rho}(0)] = \frac{i}{4}(-\rho_{xs} + \rho_{sx} - \rho_{zy} + \rho_{yz}), \quad (\text{C.11})$$

$$\text{Tr}[\hat{S}_z^A(0)\hat{S}_x^D(0)\hat{\rho}(0)] = \frac{1}{4}(\rho_{ys} + \rho_{zx} + \rho_{sy} + \rho_{xz}), \quad (\text{C.12})$$

$$\text{Tr}[\hat{S}_z^A(0)\hat{S}_y^D(0)\hat{\rho}(0)] = \frac{i}{4}(\rho_{xs} - \rho_{sx} - \rho_{zy} + \rho_{yz}). \quad (\text{C.13})$$

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