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Green's function calculation of radical pair recombination: I. Gyroscopic model formalism

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Abstract

A general gyroscopic model description of radical pair recombination in high magnetic fields is formulated. Recombination is allowed to occur simultaneously from the singlet and triplet states. The description is valid for any diffusion model, symmetry of the system, and exchange interaction, as well as for any rate of recombination, dephasing, intra-radical relaxation, and singlet–triplet mixing. By use of Green's function technique we derive general fundamental expressions for the stationary recombination probability for spherical symmetric systems with contact recombination. These general expressions can be applied to a wide class of radical pair systems and they form an exact foundation for development of systematic and consistent approximation schemes. It is shown that the recombination and escape yields for any combination of reactive channels and precursor spin states can be calculated from the singlet recombination yield for a triplet precursor. The general results are applied to a locally weak exchange interaction and explicit expressions are derived for the recombination probability in terms of contact values of the Green's function for the relative motion of the radical partners. The resulting expressions can be adopted to experimental situations by inserting the required values for the adopted diffusion model.
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1. Introduction

Magneto-spin effects on the recombination yield of geminate radical pairs (RPs) are now reasonably well understood, at least at the qualitative level, for RPs in liquid solutions and under high magnetic fields. On the quantitative level one must rely on approximate analytic solutions for simplified systems or numerical solutions. In principle, one can always obtain accurate results of these effects by numerically solving the stochastic Liouville equation (SLE) [1,2]. However, for complicated systems, considerable difficulties may arise both in obtaining a numerical solution and in its physical interpretation. Therefore, analytic solutions, even approximate but reliable ones, are important. In recent years there has been a substantial improvement in the accuracy of the theoretical solutions, but there still remain fundamental, unsolved theoretical problems of interest to the analysis of experimental data.

The theoretical methods, their advantages and short comings can be roughly classified as follows. The reencounter method [3–5] is easy to apply and exits in several variants of which one [5] is exact for a local exchange interaction while the others are more approximate but may include qualitative features of the exchange interaction. Analytic solutions are similarly easily obtained from the backward stochastic Liouville equation [6], which in addition automatically gives the dependence on the initial separation of the radicals, but again only for a local exchange interaction.

The spatial dependence of the exchange interaction has been included in the analytical calculations by two different approach. The first approach is based on the idea to split the

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spin-Hamiltonian into two parts according to the separation of the radicals; one region where the exchange interaction is dominating (and all other interactions are neglected) and another region where the exchange interaction is neglected [7]. The difficult part of the method, denoted sudden perturbation approximation, is to determine the position where the two solutions are matched. This method [7] can be used for an exponentially decaying exchange interaction of arbitrary strength but only for a locally weak singlet–triplet (S–T_0) mixing and it is not clear whether it can be generalized to confined systems.

Another approach is based on Green's function techniques and the different variants can be denoted by the applied decoupling procedure, which is either the contact approximation [8–10] or the kinematic approximation [11–13]. When applied to simple systems, these methods give rather accurate and physically interpretable results, and they can be extended to cover fairly complicated systems when combined with numerical calculations.

Green's function methods have been applied to recombination processes in two different versions. The oldest works [14,15] used the specific form of the free diffusion Green's function, while the more recent ones [9,10] are general in the sense that the derived expressions are expressed in terms of specific values of a general diffusional Green's function, i.e., without specifying the diffusion model, but still assuming a local exchange interaction. The latter, general solution [9,10] is applicable for any strength of S–T_0 mixing and spin relaxation rates and it has been used both for free diffusion models, corresponding to liquid solutions, and to micelles. A more advanced Green's function method has recently been applied to chemically induced dynamic electron polarization (CIDEP) [16,12,13,17]. It is capable of treating any strength of S–T_0 mixing for a spatially varying, locally weak exchange interaction and it has similarly been applied to both free diffusion systems [12] and to confined systems such as micelles [17]. In principle the method is capable of treating an arbitrary exchange interaction for a locally weak S–T_0 mixing.

In the present work, we extend the previous Green's function method [16,12] such that it can be used to calculate recombination yields in the presence of spin relaxation and additional dephasing processes. In order to realize the full potential of the method it is necessary to use a gyroscopic description, especially when relaxation is included. The derived general expressions are valid for any diffusion model and only require the contact values of the diffusional Green's function, which for example are known for free diffusion and micelles, or similar confined systems. The physical interpretation of the different terms is facilitated by use of effective radii, which has previously proved to be convenient [1,7]. The method is valid for arbitrary values of: S–T_0 mixing parameter, relaxation rates, and recombination decay rates through the singlet and the triplet channels. Explicit expressions are derived for a locally weak exchange interaction, which should cover many realistic situations, and e.g., are currently being used to analyze experimental data of radical pair recombination in liquids [18]. The method is, however, capable of handling much more complex systems, and the present work establishes a common platform for further treatments of special systems. Work is in progress to include a locally strong exchange interaction and even non-spherical interactions.

2. General description

Although the standard gyroscopic model representation [19] can only be used to describe the evolution of a two-level system, we will show that the present four level system can in fact be described by a very convenient, effective gyroscopic model. Our strategy is to use a gyroscopic description for the spin subspace (S, T_0) in the absence of relaxation and then add additional spin states to allow for relaxation.

The spin evolution of a RP and its associated magnetic field effects (MFE) are completely described by the stochastic Liouville equation (SLE) for the spin density matrix $\rho(q, t)$ [1]

$$\partial_t\rho(q,t) = -\mathrm{i}(\hat{\hat{H}}_0 + \hat{\hat{J}}(q))\rho(q,t) - (\hat{\hat{R}} + \hat{\hat{U}}(q))\rho(q,t) + \mathscr{L}\rho(q,t), \tag{1}$$

where q is the coordinate of the RP in the classical configuration space (typically the separation between the radicals), and $\mathscr{L}$ is a functional operator describing the stochastic motion of the RP. The Liouville representation of the decay of the RPs through the singlet and triplet channels is given by the anticommutator superoperator $\hat{\hat{U}}(q) = \frac{1}{2}\{\hat{U}(q), \cdots\}$ where

$$\hat{U}(q) = K_S(q)\hat{P} + K_T(q)\hat{Q} \tag{2}$$

and $\hat{P} = \frac{1}{4} - \hat{\mathbf{S}}_\mathrm{A}\cdot\hat{\mathbf{S}}_\mathrm{B}$ and $\hat{Q} = 1 - \hat{P} = \frac{3}{4} + \hat{\mathbf{S}}_\mathrm{A}\cdot\hat{\mathbf{S}}_\mathrm{B}$ are projection operators onto the singlet state and triplet manifold, respectively. Intra-radical relaxation of the RP is in the present work described by the usual Bloch equations and is represented by the superoperator $\hat{\hat{R}}$.

The coherent evolution of the spin system is described by the commutator generated superoperators of the RP spin-Hamiltonians in the Liouville representation, i.e., $\hat{\hat{H}}_0 = [\hat{H}_0, \cdots]$ and $\hat{\hat{J}}(q) = [\hat{J}(q), \cdots]$. For simplicity, we consider only strong magnetic fields, i.e. $B \gg a_{\mathrm{A,B}}/g_{\mathrm{A,B}}\beta$. The free spin Hamiltonian can then be written as

$$\hat{H}_0 = \omega_0(\hat{S}_{z\mathrm{A}} + \hat{S}_{z\mathrm{B}}) + \delta(\hat{S}_{z\mathrm{A}} - \hat{S}_{z\mathrm{B}}), \tag{3}$$

where the two parameters

$$\omega_0 = \frac{1}{2}(\omega_\mathrm{A} + \omega_\mathrm{B}) \quad \text{and} \quad \delta = \frac{1}{2}(\omega_\mathrm{A} - \omega_\mathrm{B}) \tag{4}$$

are expressed in terms of the effective Larmor frequencies

$$\omega_\gamma = g_\gamma\beta B + \sum_{j\in\gamma} a_j m_j, \quad \text{where } \gamma = \mathrm{A}, \mathrm{B}. \tag{5}$$

In these definitions m_j are the nuclear spin quantum numbers of the nuclear spins on radical γ. This implies that ω_0 and δ are determined by the nuclear spin configuration of

the RP which is a conserved quantity. The exchange interaction

$$\hat{J}(q) = -J(q)\left(\frac{1}{2} + 2\hat{\mathbf{S}}_{\mathrm{A}} \cdot \hat{\mathbf{S}}_{\mathrm{B}}\right). \tag{6}$$

where $2J(q)$ is the spatially dependent energy difference between the singlet and triplet states.

2.1. Gyroscopic model representation

It is well known [19] that, in the absence of spin relaxation, the coherent dynamic evolution of a single spin is a "classical" precession of the effective spin $\mathbf{S}$, about the effective magnetic field $\mathbf{B}_{\mathrm{e}}(q)$, i.e.

$$\partial_t \mathbf{S}(q,t) = \mathbf{B}_{\mathrm{e}}(q) \times \mathbf{S}(q,t). \tag{7}$$

In the absence of spin relaxation, only two electron spin states of the radicals are coupled and as a basis for this two-dimensional spin space we use the coupled electron spin states $|S\rangle$ and $|T_0\rangle$. The effective magnetic field in this representation is $\mathbf{B}_{\mathrm{e}}(q) = (2\delta, 0, 2J(q))$, and the effective spin (or polarization) vector is

$$\mathbf{S}(q,t) = \mathrm{Tr}[\rho(q,t)\hat{\sigma}], \tag{8}$$

where $\hat{\sigma}$ is a vector operator consisting of the three Pauli spin matrices σ_i $(i = x, y, z)$ in the ST_0 basis. All components of the effective spin in the ST_0 basis are real combinations of the complex matrix elements of the spin density matrix ρ_{ij}

$$\begin{aligned} S_x(q,t) &= \rho_{ST_0}(q,t) + \rho_{T_0S}(q,t), \\ S_y(q,t) &= \mathrm{i}(\rho_{ST_0}(q,t) - \rho_{T_0S}(q,t)), \\ S_z(q,t) &= \rho_{SS}(q,t) - \rho_{T_0T_0}(q,t). \end{aligned} \tag{9}$$

If singlet or triplet RPs can recombine (decay through reactive channels), then the trace of the density matrix is no longer conserved. In addition to the above three components of the effective spin vector it is necessary to include the sum of populations of the singlet and triplet T_0 states

$$S_+(q,t) = \mathrm{Tr}[\rho(q,t)] = \rho_{SS}(q,t) + \rho_{T_0T_0}(q,t) \tag{10}$$

into the description. Decay through reactive T_+ and T_- channels does not complicate the description as these states are completely decoupled from each other and the remaining states. This situation is changed, however, if spin relaxation is included.

Spin relaxation causes an incoherent mixing of almost all elements of the density matrix. But no off-diagonal element of the density matrix with one of the index equal to T_+ or T_- is created since the Hamiltonian, given by Eqs. (3) and (6), is diagonal in the T_+ and T_- states and the initial spin state of the RP is assumed to be a statistical mixture of singlet and triplet states, i.e.

$$\rho_0 = \sigma_S|S\rangle\langle S| + \sum_{j=0,+,-} \sigma_{T_j}|T_j\rangle\langle T_j|, \tag{11}$$

where

$$\sigma_S + \sigma_{T_0} + \sigma_{T_+} + \sigma_{T_-} = 1. \tag{12}$$

Consequently, it is only necessary to include the following matrix elements of the density matrix: $\{SS,\ ST_0,\ T_0S,\ T_0T_0,\ T_+T_+,$ and $T_-T_-\}$. In addition to the gyroscopic combination of matrix elements, Eqs. (9) and (10), we introduce

$$T_z(q,t) = \rho_{T_+T_+}(q,t) - \rho_{T_-T_-}(q,t), \tag{13}$$

$$T_+(q,t) = \rho_{T_+T_+}(q,t) + \rho_{T_-T_-}(q,t). \tag{14}$$

The SLE (1) in this extended gyroscopic representation now becomes a set of six coupled equations that are easily derived from the above expressions for the Hamiltonian, the recombination superoperator, and the assumption that the spin relaxation of the individual radicals can be described by Bloch equations. The spin relaxation superoperator $\hat{R}$ follows immediately from the Bloch equations for the individual radicals by formulating them in the direct product space followed by a transformation into the above defined gyroscopic basis.

The resulting equations, or rather the Laplace transformed versions, can be written as two sets of equations, cf. Appendix A. The second set of equations, Eqs. (A.2), can (in principle) be solved independently of the first set, thereby expressing S_+ and T_+ in terms of S_z; an explicit solution for contact recombination is given in Appendix A. By inserting this solution into the first set of equations, Eq. (A.1), the problem has be reduced to solving four equations.

A description based on the two set of equations, (A.1) and (A.2), is identical to the SLE (1) and can thus be applied for any motional model (e.g., diffusion) of the radicals and any functional form of the exchange interaction $J(q)$ and decay rates $K_j(q)$ $(j = S, T, d)$. However, the possibility of, and method for obtaining analytic solutions obviously depends on the complexity of the problem. In the present work, we illustrate the use of Green's function methods for the simplest, non-trivial systems.

3. Contact recombination

In order to simplify to problem without sacrificing the physical description, we will assume that the system is spherical symmetric, i.e., q is the separation between the radicals (r). Furthermore, we will use a contact representation of the decay channels, i.e.

$$K_i(r) = K_i \frac{\delta(r-d)}{4\pi r d}, \quad i = S, T, d, \tag{15}$$

where d is the distance of closest approach which may be estimated as the sum of radii of the two radicals. It is convenient to introduce a dephasing rate $K_{\mathrm{d}}(r)$ as

$$K_{\mathrm{d}}(r) \geqslant \frac{1}{2}[K_S(r) + K_T(r)], \tag{16}$$

where the inequality sign can be used to include additional dephasing sources to that of the recombination process.

The appearance of the dephasing rate in the equation of motion is shown in Appendix A.

We make no assumptions on the functional form of the exchange integral $J(r)$ in this section but, in accordance with usual practice, the two radicals of the RP is assumed to be created at contact, i.e.

$$f(r) = \frac{\delta(r-d)}{4\pi r d}. \tag{17}$$

3.1. Recombination radii

It is convenient to express the results in terms of recombination radii. They are introduced by relations similar to the usual Smoluchowski relations for classical reactions, i.e., in the absence of spin dynamics. The singlet and triplet recombination radii, R_S and R_T respectively, are defined in terms of the bimolecular rate constant K_j^{d} by the relation

$$K_j^{\mathrm{d}} = \frac{e^{-U_0}}{C_0}\frac{R_j}{d}, \quad j = S, T, \tag{18}$$

where U_0 is the value (in units of kT) at the recombination distance of a potential affecting the diffusive motion; the bulk value of the potential is set to zero. For free diffusion, the reciprocal of the contact value of Green's function equals the usual expression for the diffusion controlled rate constant, i.e., $1/C_0 = 4\pi d D$. For a general diffusion model, C_0 is defined as the contact value

$$C_0 = G(d, d; 0) \tag{19}$$

of the diffusional Green's function $G(r, r'; s)$ that satisfies

$$(s - \mathscr{L}_r)G(r, r'; s) = \frac{\delta(r-r')}{4\pi d^2}. \tag{20}$$

As usual, the rate constant can be expressed in terms of the diffusion controlled rate constant K_j^{D} and the decay rate at contact K_j as $1/K_j^{\mathrm{d}} = 1/K_j^D + e^{U_0}/K_j$. The above definition can thus be rewritten as

$$R_j = d\frac{K_j C_0}{1 + K_j C_0}, \quad j = S; T, d. \tag{21}$$

Note that the recombination radii $R_j \leqslant d$ ($j = S, T$) and that the equality sign is obtained only in the diffusion controlled limit. It may therefore also be convenient to introduce dimensionless radii, using the distance of closest approach d as unit [1,3]

$$\Lambda_j = R_j/d. \tag{22}$$

The diffusion controlled limit corresponds to $\Lambda_j = 1$. The average recombination radius will be useful later

$$\bar{R} = \frac{1}{2}(R_S + R_T), \quad \bar{\Lambda} = \frac{1}{2}(\Lambda_S + \Lambda_T). \tag{23}$$

3.2. Liouville equation

For contact recombination, the Laplace transformed stochastic Liouville equation in the gyroscopic representation can be transformed into solvable algebraic equations, cf. Appendix A. The component S_+ can be eliminated and a closed set of equations is obtained, which in matrix form can be written as

$$s\mathbf{S}(r;s) = \left(\mathbf{\Omega} + \mathbf{R} + \mathbf{J}(r) + \mathbf{K}\frac{\delta(r-d)}{4\pi r d}\right)\mathbf{S}(r;s) + \mathscr{L}_r\mathbf{S}(r;s) - \mathbf{S}_0(s)\frac{\delta(r-d)}{4\pi r d}. \tag{24}$$

The matrices are given in Appendix A, and $\mathbf{S}$ includes not only the three gyroscopic components (S_x, S_y, S_z) but also the additional component T_z. The elimination of the S_+ component gives rise to the s dependence of the last term, which would otherwise have been an initial condition. The components of $\mathbf{S}_0(s)$ are

$$S_{0x} = S_{0y} = 0, \quad S_{0z} = S_0^{\mathrm{eff}}(s), \quad T_z^0 \neq 0, \tag{25}$$

which involves an effective initial value of S_z, i.e., an effective initial population difference. In the $s \to 0$ limit, this quantity can be expressed in terms of recombination radii

$$n_0^{\mathrm{eff}} \equiv S_0^{\mathrm{eff}}(0) = \sigma_0\left[1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta\right]^{-1}, \tag{26}$$

where σ_0 is an effective initial spin state

$$\sigma_0 = (1-\Lambda_S)\sigma_S - (1-\Lambda_T)\sigma_{T_0} + (\Lambda_S - \Lambda_T)\eta\left(\sigma_{T_0} - \frac{\sigma_{T+} + \sigma_{T-}}{2}\right) \tag{27}$$

and η can be written as

$$\eta = \frac{1}{2}\frac{(C_0 - C_1)(1-\Lambda_T)}{C_0 - (C_0 - C_1)\Lambda_T}. \tag{28}$$

The quantity C_1 is another special value of the diffusional Green's function

$$C_1 = G(d, d; K_1), \tag{29}$$

where the relaxation parameters (relaxation rates) are defined as

$$\begin{aligned} K_1 &= K_{1\mathrm{A}} + K_{1\mathrm{B}} \equiv 1/T_{1\mathrm{A}} + 1/T_{1\mathrm{B}}, \\ \Delta K_1 &= 1/T_{1\mathrm{A}} - 1/T_{1\mathrm{B}}, \\ K_2 &= 1/T_{2\mathrm{A}} + 1/T_{2\mathrm{B}}. \end{aligned} \tag{30}$$

If the longitudinal relaxation times of the two radicals are equal then Eq. (24) has the same form as the previous gyroscopic model equation [16], but with an additional relaxation terms. The two former terms of Eq. (27) are identical to those found in the absence of relaxation [12]. The last term vanishes if the initial spin state of the RP is either a pure singlet, an unpolarised triplet (i.e., the three triplet sub-levels are equally populated), the singlet and triplet recombination channels are equally reactive ($\Lambda_S = \Lambda_T$), or the longitudinal relaxation is negligible ($K_1 \approx 0$ which implies $C_1 \approx C_0$ and thus $\eta \approx 0$).

The quantity η describes the efficiency of longitudinal relaxation and it is seen to depend on the reactivity of the triplet states (Λ_T). It vanishes for very slow relaxation

($K_1 \approx 0$) or very fast triplet recombination ($\Lambda_T = 1$). For infinitely fast relaxation, $\eta = \frac{1}{2}$. Only for these limiting cases, is the parameter independent of the triplet recombination. For unreactive triplets, $\eta = (C_0 - C_1)/(2C_0)$.

Since we want to calculate the stationary value of the recombination yield, i.e., the accumulated recombination yield for all times, we only need to consider the $s \to 0$ limit of Eq. (24). By introducing the stationary Green's function

$$-(\mathbf{\Omega} + \mathbf{R} + \mathbf{K}(r) + \mathscr{L}_r)\mathbf{G}^d(r, r') = \mathbf{I}\frac{\delta(r - r')}{4\pi dr}, \tag{31}$$

where $\mathbf{I}$ is the unit matrix, the stationary limit of Eq. (24) can be written in integral form as

$$\mathbf{S}(r) = \mathbf{G}^d(r, d)\mathbf{S}_0 + 4\pi \int \mathbf{G}^d(r, r')\mathbf{J}(r')\mathbf{S}(r')r'^2\, \mathrm{d}r', \tag{32}$$

where $\mathbf{S}_0$ is the stationary ($s \to 0$) value of $\mathbf{S}_0(s)$ and $\mathbf{S}(r)$ is a short hand notation for $\mathbf{S}(r; 0)$. Note that the exchange interaction $J(r)$ is not included in the definition of the Green function.

3.3. Relation between singlet and triplet yields

The singlet and triplet recombination yields can be expressed in terms of the recombination radii as (see Appendix A for a derivation)

$$\mathscr{R}_S = \frac{\frac{1}{2}\Lambda_S}{1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta}\left\{(1 - \Lambda_T) \times [(\sigma_S + \sigma_{T_0})(1 - \eta) + (\sigma_{T_+} + \sigma_{T_-})\eta] + \frac{S_z^0}{C_0}\right\}, \tag{33}$$

$$\mathscr{R}_T = \frac{\frac{1}{2}\Lambda_T}{1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta}\left\{(1 - \Lambda_S) \times (1 + \eta) + \frac{2C_1\eta}{(C_0 - C_1)}(\sigma_{T_+} + \sigma_{T_-}) - \frac{S_z^0}{C_0}\right\}, \tag{34}$$

where we have introduced the short hand notation

$$S_z^0 \equiv S_z(d, 0) = \mathbf{S}_z(d). \tag{35}$$

It is seen that the value of this quantity is all that is needed for a calculation of the recombination yield and, rather interesting, all information on the exchange interaction $J(r)$ is contained in this component. Its value is obtained by solving Eq. (32).

From Eqs. (33) and (34), we derive a new relation between the singlet and triplet recombination yields

$$\Lambda_T\mathscr{R}_S + \Lambda_S\mathscr{R}_T = \Lambda_S\Lambda_T. \tag{36}$$

The triplet recombination yield $\mathscr{R}_T$ can thus be calculated directly from the singlet recombination yield

$$\mathscr{R}_T = \Lambda_T\left(1 - \frac{\mathscr{R}_S}{\Lambda_S}\right). \tag{37}$$

The escape probability (Y) can similarly be expressed in terms of the singlet recombination probability since

$$Y = 1 - \mathscr{R}_T - \mathscr{R}_S = 1 - \Lambda_T - (\Lambda_S - \Lambda_T)\frac{\mathscr{R}_S}{\Lambda_S}. \tag{38}$$

3.4. Approximate solution procedures

The integral equations (32) for the stationary (extended) gyroscopic components in dimensional form are given in Appendix B, Eq. (B.29). This set of equations can be solved by applying an approximation scheme similar to that used for chemically induced dynamic electron polarization (CIDEP) [12]. The essence of the scheme is a decoupling procedure (closure or kinematic approximation) which is applied to the integrals in Eq. (B.29). The procedure is applicable when the exchange interaction decays fast and is locally weak [12], i.e.

$$\ell_x \ll d, \quad \text{and} \quad \left|\frac{2J_0\ell_x^2}{D}\right| \ll 1, \tag{39}$$

where ℓ_x is a characteristic length scale of the exchange interaction, cf. Appendix B. The calculation scheme can be performed with varying degree of accuracy. The simplest approximation is the so-called contact approximation, which corresponds to a delta function representation of the exchange interaction, for which the decoupling procedure is exact. In our CIDEP study [13,17] we found that this simple approximation is accurate only if the singlet–triplet (S–T_0) mixing is locally weak, i.e.

$$\frac{\delta\ell_x^2}{D} \ll 1. \tag{40}$$

If this condition is not satisfied or the dephasing is infinitely fast, then a more accurate procedure had to be used for CIDEP. An expansion in terms of the parameter ℓ_x/d was shown to give very accurate expressions both to zeroth- and first-order by comparison with numerical results [13,17]. However, it is well known that the exchange interaction plays a much more important role for CIDEP than for the recombination yield. For example, it was shown in [9] that the contact approximation of the exchange interaction gives accurate results for a locally weak exchange interaction (39) over a wide interval of values of the singlet–triplet (S–T_0) mixing parameter, including values for which condition (40) is violated.

Thus in the remaining part of this work, we will use the contact approximation for the exchange integral. By keeping the mathematics as simple as possible we can focus on the important combinations of physical parameters that make the expressions as simple and general as possible and allow for physical interpretation. By formulating the final expressions of the recombination yield in terms of effective radii, that have a clear physical meaning, we expect that the form of the expressions are general and that more advanced solution methods for more general systems will produce the same form although with different parameter values. We will continue to include additional dephasing processes since it facilitates the important distinction of the two effects of the recombination process: disappearance of radicals and dephasing of quantum states.

4. Recombination for contact exchange

In this and the following sections, we apply dimensionless parameters. The definitions are given in Appendix B but all that is needed for now is that the dimensional and dimensionless parameters are denoted with the same letter, in upper and lower cases respectively. For a contact exchange interaction, $j(x) = j_e\delta(x)$, the basic integral equations Eq. (B.29) reduces to a simple set of linear algebraic equations which is easily solved. Assuming the initial precursor state is an unpolarized triplet, the result for the needed z component can be written as

$$s_z^T(0) = -\frac{1}{3(1+k_T c_0)}\frac{M(1+k_e c_0(1+\eta)-k_T c_0\eta)}{1+k_e M}, \tag{41}$$

where

$$M = \frac{a_0 + (a_0^2+b_0^2)k_j}{1+a_0 k_j} \tag{42}$$

has been introduced in accordance with [9], but for the more general case of additional dephasing processes. A similar expression can be derived for a singlet precursor but, as shown below, the quantity for a singlet precursor can be derived very simple from that of an unpolarized triplet, cf. Eq. (53). The quantity M depends explicitly on the internal spin dynamics through the special contact values of the diffusional Green's function, a_0 and b_0, defined in Eq. (B.26), but has no explicit dependence on the singlet or triplet reactivities. It does, however, depend on dephasing processes through k_j, defined below, and this quantity contains the dephasing constant k_d, which depends on the decay rates through the reactive channels, cf. Eq. (16).

The total dephasing rate constant is

$$k_j = j_e^2 g_T + k_d, \tag{43}$$

where

$$g_T = \frac{1}{2}\frac{c_A + c_B + 2k_T c_A c_B}{1+\frac{1}{2}(k_d+k_T)(c_A+c_B)+k_d k_T c_A c_B}. \tag{44}$$

The quantities c_A and c_B are contact values of the diffusional Green's function that depend on the longitudinal relaxation rates of the two radicals (A and B). It is interesting to note that the effect of the dephasing processes occurs only through this combination. The presence of j_e was expected, considering the dephasing effect of the exchange interaction, but the precise appearance was previously unknown.

Eq. (43) shows that both exchange and decay through reactive channels contribute to dephasing. However, if the dephasing is instantaneous ($k_j \to \infty$) due to strong exchange, then the dephasing becomes independent of the reactivities. On the other hand, if the exchange dephasing is negligible then dephasing is determined solely by the reactivities. All other cases are intermediate to these limiting cases, which allows us to study the maximal effect of dephasing on the recombination yield.

4.1. Dephasing radius

In order to clarify the situation, consider the particular case of infinitely slow longitudinal relaxation, i.e., $k_{1A} = k_{1B} = k_1 = 0$. In that case $c_A = c_B = c_0$, and it follows from Eq. (44) that:

$$g_T = \frac{c_0}{1+k_d c_0}, \tag{45}$$

and the dephasing combination in Eq. (43) becomes

$$k_j^0 = \lim_{k_1\to 0} k_j = k_d + \frac{j_e^2 c_0}{1+k_d c_0}. \tag{46}$$

A dephasing radius R_{T_0S} can be introduced, similarly to Eq. (21), as

$$\frac{R_{T_0S}}{d} = \frac{(k_d + \mathrm{i}j_e)c_0}{1+(k_d+\mathrm{i}j_e)c_0}, \tag{47}$$

$$= \frac{k_d c_0(1+k_d c_0) + j_e^2 c_0^2 + \mathrm{i}j_e c_0}{(1+k_d c_0)^2 + j_e^2 c_0^2}. \tag{48}$$

The only difference from Eq. (21) is that the real reaction constants is replaced by the quantity $k_d + \mathrm{i}j_e$, which is complex due to the quantum mechanical nature of the exchange interaction. The real part can easily be rewritten to

$$\frac{\Re(R_{T_0S})}{d} = \frac{k_j^0 c_0}{1+k_j^0 c_0}, \tag{49}$$

since $k_j = k_j^0$ in the absence of longitudinal relaxation. The real part of the dephasing radius is similar to the usual definition of effective radii, Eq. (21). However, the effective dephasing constant k_j, given by Eq. (43), includes the exchange interaction in a non-trivial way, due to its quantum character. For a negligible exchange interaction ($j_e = 0$), Eq. (49) reduces to the defining equation for R_d.

Eq. (49) can be inverted, yielding k_j^0 in terms of the real part of the dephasing radius

$$k_j^0 = \frac{1}{c_0}\frac{\Re(R_{T_0S})/d}{1-\Re(R_{T_0S})/d}. \tag{50}$$

If the longitudinal relaxation is not infinitely slow, the definition of the dephasing radius has to be changed. However, the presence of the universal combination (43) in the expression for M, Eq. (42), unambiguously shows that this combination is precisely the combination of the real part of the dephasing radius shown in Eq. (50). An exact expression for the dephasing radius and its relation with the universal combination in Eq. (43) for a finite longitudinal relaxation rate will be derived elsewhere.

4.2. Singlet recombination

We now consider a situation where only recombination from the singlet state is observable, but both channels, singlet and triplets, may be reactive. The initial precursor state is either a pure singlet or an unpolarized triplet. Several special cases will be considered, and although the general

expression is valid for all situations, it is convenient to rewrite the expressions according to the specific application.

4.3. Relationship between singlet and triplet precursor

For a singlet precursor ($\sigma_S = 1$), Eq. (33) yields

$$\mathscr{R}_S^S = \frac{\frac{1}{2}\Lambda_S}{1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta}\left\{(1 - \Lambda_T)(1 - \eta) + \frac{s_z^S(0)}{c_0}\right\}, \tag{51}$$

while an unpolarized triplet precursor ($\sigma_S = 0$, and $\sigma_{T_0} = \sigma_{T_+} = \sigma_{T_-} = \frac{1}{3}$) gives

$$\mathscr{R}_S^T = \frac{\frac{1}{2}\Lambda_S}{1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta}\left\{\frac{1}{3}(1 - \Lambda_T)(1 + \eta) + \frac{s_z^T(0)}{c_0}\right\}. \tag{52}$$

The upper index indicates the precursor type. According to the general Eq. (B.31), the value $s_z(0)$ is proportional to n_0^{eff} for both precursor states. Thus, we see from Eqs. (26) and (27) that the following general relation holds:

$$(1 - \Lambda_S)s_z^T(0) = -\frac{1}{3}(1 - \Lambda_T)s_z^S(0). \tag{53}$$

From this result, it can readily be proved that Eqs. (51) and (52) lead to

$$(\mathscr{R}_S^S - \Lambda_S)(1 - \Lambda_T) = -3\mathscr{R}_S^T(1 - \Lambda_S). \tag{54}$$

This result is a generalization of the relation for pure singlet recombination discovered by Pedersen and Freed [1] by analyzing their numerical results, and later derived in [9]. Consequently, we only need to calculate the singlet recombination yield from a triplet precursor.

4.4. General results

The singlet recombination yield for a triplet precursor can be written as

$$\mathscr{R}_S^T = \frac{1}{3}\Lambda_S(1 - \Lambda_T)\frac{g_{\text{eff}}^S}{1 + g_{\text{eff}}^S(1 - \Lambda_S)}, \tag{55}$$

where

$$g_{\text{eff}}^S = \frac{c_0(1 + \eta) - M(1 - \eta\Lambda_T/(1 - \Lambda_T))}{c_0(1 - \eta)(1 - \Lambda_T) + M(1 + \Lambda_T(1 - \eta))}. \tag{56}$$

The meaning of the upper index S will be clear in the following. Note that the quantity g_{eff}^S does not depend explicitly on the singlet recombination (Λ_S). It only depends implicitly on the singlet reactivity through its dephasing effect, which is contained in M. The quantity can be given a clear physical interpretation. For diffusion controlled singlet recombination ($\Lambda_S = 1$), it is easily seen that

$$\mathscr{R}_S^T = \frac{1}{3}(1 - \Lambda_T)g_{\text{eff}}^S. \tag{57}$$

The second factors is the survival probability of the initial triplet radical pair in the absence of singlet–triplet mixing. One third of the surviving RPs are in the T_0 state. The last factor is therefore the irreversible transitions into the singlet state caused by S–T mixing, both coherent and incoherent (relaxation).

It is interesting to note that a simplified version of Eq. (55) was found by Pedersen and Freed [1] by analyzing their numerical results for pure singlet recombination ($\Lambda_T = 0$) and in the absence of relaxation. They called g_{eff}^S for $\mathscr{F}^*$ and interpreted this quantity as the diffusion controlled singlet recombination probability for an initial T_0 precursor, which is in agreement with the present more general relation. They also found that this quantity depended on the strength of the exchange interaction.

For very fast relaxation ($k_1, k_2 \to \infty$, implying $\eta = \frac{1}{2}$ and $M = 0$), Eq. (56) gives $g_{\text{eff}}^S = 3/(1 - \Lambda_T)$ and it thus follows from Eq. (55) that:

$$\mathscr{R}_S^T = \frac{\Lambda_S(1 - \Lambda_T)}{4 - \Lambda_T - 3\Lambda_S}. \tag{58}$$

The recombination yield vanish if the decay through the triplet channel is infinitely fast ($\Lambda_T = 1$). On the other hand, if the triplet decay rate is finite and the singlet decay is infinitely fast ($\Lambda_S = 1$), then the recombination yield is unity. If the decay rates are equal ($\Lambda_S = \Lambda_T = \bar{\Lambda}$), then

$$\mathscr{R}_S^T = \frac{\bar{\Lambda}}{4}. \tag{59}$$

These limiting results, some of which are physically obvious, follow immediately from the general expressions without specifying the diffusion model.

The singlet recombination yield for a singlet precursor can be obtained by use of the relationship (54)

$$\mathscr{R}_S^S = \frac{\Lambda_S}{1 + g_{\text{eff}}^S(1 - \Lambda_S)}. \tag{60}$$

The physically evident result, $\mathscr{R}_S^S = 1$ for diffusion controlled singlet recombination, is immediately seen to be satisfied.

The general results, Eqs. (55) and (56), together with the relationships, Eq. (37), between the singlet and triplet recombination yield, and the precursor dependence, Eq. (54), completely describes all situations for contact exchange. However, for a few special cases it is sometimes convenient to rewrite the formulas slightly. For illustration, this as done below.

4.5. Special cases

4.5.1. Fast triplet recombination

Diffusion controlled triplet recombination $\Lambda_T = 1$ implies $\eta = 0$, see Eq. (28)). The singlet recombination yield for a triplet precursor $\mathscr{R}_S^T$ is obviously zero. However, the singlet recombination yield for a singlet precursor will in general be non-vanishing and is given by Eq. (60) with

$$2g^S_{\text{eff}} = \frac{c_0}{M} - \left(1 - \frac{(c_0 - c_1)}{2c_1}\right), \tag{61}$$

$$= \frac{c_0(1 + a_0(k_\text{d} + j_\text{e}^2 g_T))}{a_0 + (a_0^2 + b_0^2)(k_\text{d} + j_\text{e}^2 g_T)} + \frac{c_0 - 3c_1}{2c_1}, \tag{62}$$

where

$$g_T = \frac{2c_\text{A}c_\text{B}}{c_\text{A} + c_\text{B} + 2k_\text{d}c_\text{A}c_\text{B}}. \tag{63}$$

Note that this result is different from that discussed below for no relaxation, although $\eta = 0$ in both cases, since relaxation is included also in the term $(c_0 - c_1)/(2c_1)$.

4.5.2. No T_1 relaxation

Infinitely slow relaxation ($k_1 \approx 0$) implies $\eta = 0$ just as in the previous example. However, for a finite triplet recombination rate, Eq. (56) yields

$$g^S_{\text{eff}} = \frac{c_0 - M}{c_0 + M + (M - c_0)\Lambda_T}, \tag{64}$$

where M is given by Eq. (42) but now with g_T given by Eq. (45). This expression evaluated for infinitely fast triplet recombination ($\Lambda_T = 1$) coincides with Eq. (61) for $k_1 = 0$, as it should, but in general this quantity depends explicitly on the triplet recombination (Λ_T). It may therefore be convenient to introduce a new quantity

$$g^T_{\text{eff}} = \frac{g^S_{\text{eff}}}{1 + (1 + \Lambda_T)g^S_{\text{eff}}} \tag{65}$$

that does not depend explicitly on either of the reactivities (Λ_T or Λ_S). It can be evaluated to

$$g^T_{\text{eff}} = \frac{1}{2}\left(1 - \frac{M}{c_0}\right) = \frac{1}{2c_0}(c_0 - M). \tag{66}$$

The singlet recombination yield for an unpolarized triplet precursor can now be written as

$$\mathscr{R}^T_S = \frac{1}{3}\frac{\Lambda_S(1 - \Lambda_T)g^T_{\text{eff}}}{1 - g^T_{\text{eff}}(\Lambda_S + \Lambda_T)}. \tag{67}$$

4.5.3. Unreactive triplet states

For unreactive triplets ($\Lambda_T = 0$), we have from Eq. (56)

$$g^S_{\text{eff}} = \frac{c_0(1 - \eta) - M}{c_0(1 - \eta) + M}, \tag{68}$$

but an alternative convenient quantity is

$$g^T_{\text{eff}} = \frac{g^S_{\text{eff}}}{1 + g^S_{\text{eff}}} \tag{69}$$

defined by the transformation Eq. (65) for the particular case of $\Lambda_T = 0$. The singlet recombination yield can then be written as

$$\mathscr{R}^T_S = \frac{1}{3}\frac{g^T_{\text{eff}}\Lambda_S}{1 - g^T_{\text{eff}}\Lambda_S}. \tag{70}$$

This new quantity can be evaluated to

$$g^T_{\text{eff}} = \frac{1}{2}\left(1 + \eta - \frac{M}{c_0}\right) = \frac{1}{4c_0}\{3c_0 - c_1 - 2M\}, \tag{71}$$

where

$$g_T = \frac{1}{2}\frac{c_\text{A} + c_\text{B}}{1 + \frac{1}{2}k_\text{d}(c_\text{A} + c_\text{B})}, \tag{72}$$

As for the previous case of no relaxation, M and thus g^T_{eff} does not depend explicitly on the rate of recombination through the recombination channels. But, as before they implicitly depend on the recombination rate through the dephasing rate k_j. When relaxation is negligible ($\eta = 0$), Eq. (71) reduces to Eq. (66). Notice, however, that Eq. (71) cannot be used in Eq. (67). When both relaxation and triplet recombination is present, only Eqs. (55) and (56) can be used.

5. Discussion

The main purpose of the present work has been to establish a common theoretical platform that can be used to derive analytic expressions for spin dependent recombination of radical pairs in complex systems.

The gyroscopic representation is quite general and can be used to non-spherical system with a finite range of the exchange interaction. It will allow us to construct an approximation scheme for a locally strong exchange interaction for all values of the singlet triplet mixing parameter, which previously has not been possible. Furthermore, future treatments of more general systems might confirm our expectations that the present form of the resulting expressions have a universal structure, which would significantly simplify generalizations of the results to other, more complicated systems.

The derived general relationships significantly simplify applications of the results to explicit systems, both theoretical calculations of recombination or escape yields and quantitative interpretations of experimental data. The new relation between the singlet and triplet recombination yield, Eq. (37), implies that it is sufficient to calculate the singlet yield. The relation between the singlet recombination yields for singlet and triplet precursors, Eq. (54), implies that it is sufficient to consider the singlet yield from a triplet precursor. Finally, Eq. (55) gives an explicit dependence of the recombination yield in terms of the reactivity of the singlet state, i.e., it is only necessary to calculate one spin dependent quantity, g^S_{eff}, to cover all situations.

For contact recombination and exchange interaction, the specific results of the present work agree with those obtained by a previous, different Green's function method [9,10] for the systems treated therein, i.e., for unreactive triplet states. A discussion of the accuracy and applicability of earlier methods may be found in these works [9,10]. The main advantages of the present ap-

proach to the previous Green's function method [9,10] are: that simultaneous recombination through the singlet and triplet channels are included, that the introduction of effective radii simplifies the expressions, and that the parameters are grouped together in physically meaningful combinations that displays the general structure of the solutions.

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Appendix A. Solution of Eq. (A.2)

The SLE (1) in the extended gyroscopic representation is a set of six coupled equations. However, the resulting equations, or rather the Laplace transformed versions, can be written as two sets of equations. The first set is

$$\begin{aligned}
sS_x(q,s) &= -\left[\frac{1}{2}K_1 + K_{\mathrm{d}}(q) + \mathscr{L}_q\right]S_x - 2J(q)S_y - \frac{1}{2}\Delta K_1 T_z,\\
sS_y(q,s) &= 2J(q)S_x - [K_2 + K_{\mathrm{d}}(q) + \mathscr{L}_q]S_y - 2\delta S_z,\\
sS_z(q,s) &= S_z^{\circ}(q) - [K_2 + \frac{1}{2}(K_S(q) + K_T(q)) + \mathscr{L}_q]S_z\\
&\quad + 2\delta S_y - \frac{1}{2}[K_S(q) - K_T(q)]S_+,\\
sT_z(q,s) &= T_z^{\circ}(q) - \left[\frac{1}{2}K_1 + K_T(q) + \mathscr{L}_q\right]T_z - \frac{1}{2}\Delta K_1 S_x
\end{aligned} \tag{A.1}$$

and the second set is

$$\begin{aligned}
sS_+(q,s) &= S_+^{\circ}(q) - \frac{1}{2}[K_1 + K_S(q) + K_T(q)]S_+\\
&\quad + \mathscr{L}_q S_+ - \frac{1}{2}[K_S(q) - K_T(q)]S_z + \frac{1}{2}K_1 T_+,\\
sT_+(q,s) &= T_+^{\circ}(q) - \left[\frac{1}{2}K_1 + K_T(q) + \mathscr{L}_q\right]T_+ + \frac{1}{2}K_1 S_+.
\end{aligned} \tag{A.2}$$

Eq. (A.2) can be solved by introduction of the quantities

$$A_{\pm}(q,s) = S_+(q,s) \pm T_+(q,s), \tag{A.3}$$

which transform Eq. (A.2) into

$$\begin{aligned}
sA_+(q,s) &= -\frac{1}{4}(K_S(q) + 3K_T(q))A_+(q,s) + \mathscr{L}_q A_+(q,s)\\
&\quad - \frac{1}{4}(K_S(q) - K_T(q))A_-(q,s)\\
&\quad - \frac{1}{2}(K_S(q) - K_T(q))S_z(q,s) + (S_+^0(q) + T_+^0(q))
\end{aligned} \tag{A.4}$$

and

$$\begin{aligned}
(s + K_1)A_-(q,s) &= -\frac{1}{4}(K_S(q) + 3K_T(q))A_-(q,s)\\
&\quad + \mathscr{L}_q A_-(q,s) - \frac{1}{4}(K_S(q) - K_T(q))A_+(q,s)\\
&\quad - \frac{1}{2}(K_S(q) - K_T(q))S_z(q,s)\\
&\quad + (S_+^0(q) - T_+^0(q)).
\end{aligned} \tag{A.5}$$

By introducing the Green's function by

$$[s + \frac{1}{4}(K_S(q) + 3K_T(q)) - \mathscr{L}_q]G_R(q,q';s) = \delta(q - q'), \tag{A.6}$$

assuming contact reactivity

$$K_i(q) \equiv K_i(r) = K_i\frac{\delta(r-d)}{4\pi r d} \quad \text{for} \quad i = S, T \tag{A.7}$$

and utilizing a contact initial condition

$$\sigma_(q) \equiv \sigma_i(r) = \sigma_i\frac{\delta(r-d)}{4\pi r d} \quad \text{for} \quad i = S, T_0, T_+, T_-, \tag{A.8}$$

we obtain in the stationary ($s \to 0$) limit

$$\begin{aligned}
A_+(d) &= G_R(d,d;0)\left\{1 - \frac{1}{4}(K_S - K_T)(A_-(d) + 2S_z(d))\right\},\\
A_-(d) &= G_R(d,d;0)\left\{\Delta_1 - \frac{1}{4}(K_S - K_T)(A_+(d) + 2S_z(d))\right\},
\end{aligned} \tag{A.9}$$

where

$$\Delta_1 = \sigma_S + \sigma_{T_0} - \sigma_{T_+} - \sigma_{T_-}. \tag{A.10}$$

The Green's function $G_R(d, d; s)$ can be expressed in terms of the free Green's function $G(d, d; s)$, defined in Eq. (20), as

$$G_R(d,d;s) = \frac{G(d,d;s)}{1 + \frac{1}{4}(K_S + 3K_T)G(d,d;s)}. \tag{A.11}$$

By substituting this equation into Eq. (A.9) the quantities $A_{\pm}(d)$ are determined by solving the resulting set of equations. Then by Eq. (A.3) we find the original quantities $S_+(d, 0) = S_+(d)$ and $T_+(d, 0) = T_+(d)$ in terms of the recombination constants K_S and K_T and the population difference $S_z(d)$. Substitution of these results into Eq. (A.1) gives Eq. (24), where the matrices are

$$\mathbf{\Omega} + \mathbf{J}(r) = \begin{pmatrix} 0 & -2J(r) & 0 & 0\\ 2J(r) & 0 & -2\delta & 0\\ 0 & 2\delta & 0 & 0\\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{A.12}$$

$$\mathbf{K} = \begin{pmatrix} -K_{\mathrm{d}} & 0 & 0 & 0\\ 0 & -K_{\mathrm{d}} & 0 & 0\\ 0 & 0 & -K_{\mathrm{e}} & 0\\ 0 & 0 & 0 & -K_T \end{pmatrix} \tag{A.13}$$

and

$$\mathbf{R} = \begin{pmatrix} -\frac{1}{2}K_1 & 0 & 0 & -\frac{1}{2}\Delta K_1 \\ 0 & -K_2 & 0 & 0 \\ 0 & 0 & -K_2 & 0 \\ -\frac{1}{2}\Delta K_1 & 0 & 0 & -\frac{1}{2}K_1 \end{pmatrix}. \tag{A.14}$$

The quantity K_e is defined as

$$K_e = \frac{K_S + K_T + 2K_S K_T C_0 - K_T(K_S - K_T)C_0\eta}{2 + (K_S + K_T)C_0 - (K_S - K_T)C_0\eta} \tag{A.15}$$

and can be interpreted as a kind of effective recombination constant (in the gyroscopic representation). It can be expressed in terms of the effective radii by the relation

$$[1 + (K_e + (K_e - K_T)\eta)C_0]^{-1} = 1 - \bar{\Lambda} - \frac{1}{2}(\Lambda_S - \Lambda_T)\eta. \tag{A.16}$$

Eqs. (33) and (34) for the recombination yield through the singlet and triplet channels, respectively, are found by substituting the values of T_+ and S_+ into the usual definition of the the recombination yield

$$\mathscr{R}_S = \int_0^\infty K_S \rho_{SS}(d,t)\,\mathrm{d}t = K_S \frac{S_+(d) + S_z(d)}{2},$$
$$\mathscr{R}_T = \int_0^\infty K_S \rho_{TT}(d,t)\,\mathrm{d}t = K_T\left(\frac{S_+(d) - S_z(d)}{2} + T_+(d)\right) \tag{A.17}$$

followed by elimination of K_e using Eq. (A.16), and introduction of the definitions of the recombination radii, Eq. (21).

Appendix B. Relations between the Green's functions $\mathbf{G}^d(r, r')$ and $G(r, r')$

The matrix Green function in Eq. (32) has the structure

$$\mathbf{G}^d(r,r') = \begin{pmatrix} G^d_{11}(r,r') & 0 & 0 & G^d_{14}(r,r') \\ 0 & A_e(r,r') & -B_d(r,r') & 0 \\ 0 & B_e(r,r') & A_d(r,r') & 0 \\ G^d_{41}(r,r') & 0 & 0 & G^d_{44}(r,r') \end{pmatrix}. \tag{B.1}$$

Using the contact character of the spatially dependent dissipative processes (cf. Eqs. (15) and (A.13))

$$\mathbf{K}(r) = \mathbf{K}\frac{\delta(r-d)}{4\pi r d} \tag{B.2}$$

and the Lippmann–Schwinger equation

$$\mathbf{G}^d(r,r') = \mathbf{G}(r,r') + \mathbf{G}(r,d)\mathbf{K}\mathbf{G}^d(d,r') \tag{B.3}$$

the matrix elements of the Green's function $\mathbf{G}^d(r, r')$, Eq. (B.1), can be expressed in terms of the free Green's function matrix $\mathbf{G}(r, r')$ that satisfy

$$-(\mathbf{\Omega} + \mathbf{R} + \mathscr{L}_r)\mathbf{G}(r,r') = \mathbf{I}\frac{\delta(r-r')}{4\pi d r}, \tag{B.4}$$

By inspection of Eq. (B.4) and noticing the structure of the matrices, cf. Eqs. (A.12)–(A.14) at $J = 0$, it is seen that the solution can be written as

$$\mathbf{G}(r,r') = \begin{bmatrix} G^+(r,r') & 0 & 0 & G^-(r,r') \\ 0 & A(r,r') & -B(r,r') & 0 \\ 0 & B(r,r') & A(r,r') & 0 \\ G^-(r,r') & 0 & 0 & G^+(r,r') \end{bmatrix}, \tag{B.5}$$

where

$$G^+(r,r') = \frac{1}{2}(G(r,r';K_{1A}) + G(r,r';K_{1B})),$$
$$G^-(r,r') = \frac{1}{2}(G(r,r';K_{1A}) - G(r,r';K_{1B})), \tag{B.6}$$
$$A(r,r') = \Re G(r,r';K_2 - 2\mathrm{i}\delta),$$
$$B(r,r') = \Im G(r,r';K_2 - 2\mathrm{i}\delta) \tag{B.7}$$

and $G(r, r'; s)$ is the diffusional Green's function defined in Eq. (20). Notice that the additional element in the extended gyroscopic description is decoupled from the three standard elements if the radicals have identical longitudinal relaxation times, which implies that $G^- = 0$.

In order to keep the notation as compact as possible we introduce the following notation for the special parameter values of the free Green's function:

$$C_i = G(d,d;K_{1i}), \quad \text{where } i = A, B,$$
$$A_0 = A(d,d), \quad B_0 = B(d,d). \tag{B.8}$$

By substituting Eq. (B.5) into Eq. (B.3) and solving the resulting matrix equations we derive Eq. (B.1). The contact values of the matrix elements of this matrix solution are

$$A_d = A_d(d,d) = \frac{1}{\Lambda_e}[A_0 + K_d(A_0^2 + B_0^2)],$$
$$A_e = A_e(d,d) = \frac{1}{\Lambda_e}[A_0 + K_e(A_0^2 + B_0^2)], \tag{B.9}$$
$$B_d = B_d(d,d) = B_e(d,d) = \frac{B_0}{\Lambda_e},$$

where

$$\Lambda_e = 1 + (K_d + K_e)A_0 + K_d K_e(A_0^2 + B_0^2). \tag{B.10}$$

The other matrix elements are

$$G^d_{11} = \frac{1}{2\Lambda_d}[C_A + C_B + 2K_T C_A C_B] \equiv G_T,$$
$$G^d_{44} = \frac{1}{2\Lambda_d}[C_A + C_B + 2K_d C_A C_B] \equiv G_d,$$
$$G^d_{14} = G^d_{41} = \frac{1}{2\Lambda_d}[C_A - C_B] \equiv G_0, \tag{B.11}$$

where

$$\Lambda_d = 1 + \frac{1}{2}(K_d + K_T)(C_A + C_B) + K_d K_T C_A C_B. \tag{B.12}$$

B.1. Dimensionless parameters and variables

As unit of length we use a characteristic length of the exchange interaction, ℓ_x, e.g. the decay length of an exponentially decaying interaction

$$J(r) = J_0 e^{-(r-d)/\ell_x}. \tag{B.13}$$

Dimensionless time and Laplace variables are defined as

$$\tau = t\frac{D}{\ell_x^2}, \quad p = s\frac{\ell_x^2}{D}. \tag{B.14}$$

If the diffusion coefficient D is spatially dependent it is the value of the relative diffusion coefficient at contact that is used in these definitions.

For discussing the validity regions of various approximations, it is convenient to introduce a set of characteristic dimensionless parameters. The characteristic times in the exchange region for a single encounter, for all encounters, and the characteristic reencounter time are given by

$$\tau_c = \frac{\ell_x^2}{D}, \quad \tau_e = \frac{d\ell_x}{D}, \quad \tau_d = \frac{d^2}{D}. \tag{B.15}$$

The corresponding average strengths of the quantum mechanical mixing are

$$\xi = \sqrt{\delta\tau_c} = \sqrt{\frac{\delta\ell_x^2}{D}} \quad \text{and} \quad q = \delta\tau_d = \delta\frac{d^2}{D} = \left(\frac{d}{\ell_x}\right)^2 \xi^2. \tag{B.16}$$

The local and integral strength of the exchange interaction are

$$j_c = 2|J_0|\tau_c = 2|J_0|\frac{\ell_x^2}{D} \quad \text{and} \quad j_e = 2|J_0|\tau_e = 2|J_0|\frac{d\ell_x}{D}. \tag{B.17}$$

The decay constants through the reactive and dephasing channels are scaled with the (free) diffusion controlled rate constant $K_D = 4\pi dD$,

$$k_i = \frac{K_i}{K_D} = \frac{K_i}{4\pi dD}, \quad i = S, T, d, \tag{B.18}$$

while the relaxation rates are scaled with the characteristic time in the exchange region

$$k_i = K_i\frac{\ell_x^2}{D}, \quad i = 1, 2, \tag{B.19}$$

$$k_{i\gamma} = K_{i\gamma}\frac{\ell_x^2}{D} = \frac{\ell_x^2}{T_{i\gamma}D}, \qquad i = 1, 2, \quad \gamma = \mathrm{A}, \mathrm{B}. \tag{B.20}$$

The dimensionless distance between the radicals is defined as

$$x = \frac{r-d}{\ell_x}, \tag{B.21}$$

which implies that an exponentially decaying exchange interaction can be written as

$$j(x) = j_e\, \mathrm{e}^{-x}. \tag{B.22}$$

The dimensionless form of the gyroscopic vector components are

$$s_j(x) = K_D\frac{r}{d}S_j(r), \quad j = x, y, z, \qquad t_z(x) = K_D\frac{r}{d}T_z(r) \tag{B.23}$$

and the dimensionless form of any Green's function

$$g(x, x'; p) = K_D\frac{rr'}{d}G(r, r'; s). \tag{B.24}$$

The dimensionless values of the particular quantities introduced in Eq. (19) are indicated by the same symbol, but using lower case letters. The previous equations are easily transformed into dimensionless form simply by replacing quantities denoted by capital letters by the corresponding lower case letters, and replacing the spatial variable r by x.

Bu using the usual trick of including the r factor in the Green function, the Laplace operator (∇^2) is transformed into a second derivative. The transformed version of a general diffusion operator $\mathscr{L}_r$ is denoted λ_x; and for free diffusion this is just $\lambda_x = \mathrm{d}^2/\mathrm{d}x^2$.

In dimensionless form, the defining equation for the diffusional Green's function is

$$(p - \lambda_x)g(x, y; s) = \frac{\ell_x}{d}\delta(x - y), \tag{B.25}$$

where the following values of p are of interest, $p = 0$, k_1, k_{1A}, k_{1B}, $k_2 - i2\xi^2$. The corresponding contact values, using the compact notation $g(p) \equiv g(0, 0, p)$, are

$$c_0 = g(0), \quad c_1 = g(k_1), \tag{B.26}$$

$$c_A = g(k_{1A}), \quad c_B = g(k_{1B}), \tag{B.27}$$

$$a_0 = \Re g(k_2 - 2i\xi^2), \quad b_0 = \Im g(k_2 - 2i\xi^2). \tag{B.28}$$

The integral equations (32) for the stationary (extended) gyroscopic components can be written as

$$\begin{aligned}
s_x(x) &= g_{14}^d(x, 0)(\sigma_{T_+} - \sigma_{T_-}) - \int g_{11}^d(x, y)j(y)s_y(y)\,\mathrm{d}y,\\
s_y(x) &= -b_d(x, 0)n_0^{\mathrm{eff}} + \int a_e(x, y)j(y)s_x(y)\,\mathrm{d}y,\\
s_z(x) &= a_d(x, 0)n_0^{\mathrm{eff}} + \int b_e(x, y)j(y)s_x(y)\,\mathrm{d}y,\\
t_z(x) &= g_{44}^d(x, 0)(\sigma_{T_+} - \sigma_{T_-}) - \int g_{41}^d(x, y)j(y)s_y(y)\,\mathrm{d}y,
\end{aligned} \tag{B.29}$$

where the dimensionless parameters and variables are obtained by replacing capital letters with the corresponding lower case ones. It is interesting to note that the first three equations forms a closed set that are decoupled from the last equation.

For a contact exchange interaction, $j(x) = j_e\delta(x)$, Eq. (B.29) reduces to a simple set of linear algebraic equations

$$\begin{aligned} s_x(0) &= g_0(\sigma_{T_+} - \sigma_{T_-}) - j_e g_T s_y(0), \\ s_y(0) &= -b n_0^{\text{eff}} + a_e j_e s_x(0), \\ s_z(0) &= a_d n_0^{\text{eff}} + b j_e s_x(0) \end{aligned} \tag{B.30}$$

that are easily solved to give

$$s_z(0) = \frac{[a_d + j_e^2 g_T (a_d a_e + b^2)] n_0^{\text{eff}} - j_e g_0 b (\sigma_{T_+} - \sigma_{T_-})}{1 + j_e^2 g_T a_e}. \tag{B.31}$$

By use of Eqs. (B.9) and (B.10) this result can be rewritten to

$$s_z(0) = \frac{[a_0 + (a_0^2 + b_0^2)(k_d + j_e^2 g_T)] n_0^{\text{eff}} - j_e g_0 b_0 (\sigma_{T_+} - \sigma_{T_-})}{1 + k_e a_0 + (k_d + j_e^2 g_T)(a_0 + k_e (a_0^2 + b_0^2))}. \tag{B.32}$$

This results is then reformulated into Eq. (41).

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