

Ensemble averaged spin pair dynamics of doublet and triplet molecules

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Analytical expressions are presented which describe the spin dynamics of random ensembles of pairs of molecules, the partners being either of doublet (2D) or of triplet (3T) type. The spin dynamics are induced either by the hyperfine coupling (2D) or by the zero-field splitting (3T). The three spin transitions $^1(^2D_1 + ^2D_2) \rightarrow ^3(^2D_1 + ^2D_2)$, $^4(^3T_1 + ^2D_2) \rightarrow ^2(^3T_1 + ^2D_2)$, and $^{3,5}(^3T_1 + ^3T_2) \rightarrow ^1(^3T_1 + ^3T_2)$ are considered at low and high magnetic fields. The ensemble average is taken over all nuclear spin configurations (2D), over all molecular orientations (3T) and over possible histories which may include nuclear spin realignments by paramagnetic-diamagnetic exchange (2D) or molecular reorientations by rotational diffusion or exciton migration in random matrices (3T). The results obtained demonstrate that magnetic fields influence the processes of triplet quenching by radicals and triplet-triplet annihilation and thereby can provide information on the rotational diffusion of triplet molecules, exciton migration, and paramagnetic-diamagnetic exchange. Such effects predicted earlier by us for processes involving doublets [J. Chem. Phys. 71, 1878 (1979)] and discussed here, were recently demonstrated experimentally [F. Nolting, H. Staerk, and A. Weller, Chem. Phys. Lett. 88, 523 (1983)]. The results presented are also of general interest as the spin systems considered provide a solvable model to describe the degree of randomization in ensembles of quantum systems.

I. INTRODUCTION

In this article we consider three bimolecular processes which are influenced by external magnetic fields in the range of a few Gauss to a few Tesla: radical pair recombination,¹ triplet quenching by radicals,² and triplet-triplet annihilation.³ These processes involve molecules with an electron spin of doublet or triplet character.

Ordinarily one does not expect that molecular processes in condensed matter at higher temperatures will be influenced by magnetic interaction energies which are much smaller than thermal energies. If, however, a molecular reaction at a decisive intermediate stage is not subject to fast thermal relaxation, i.e., if the reaction proceeds by a coherent quantum process, then magnetic interactions can indeed play a role. For this to be true, the magnitude of the Zeeman interaction between electron spins and external fields of 10 – 10^4 G implies that the intermediate quantum process should last between 10^{-8} – 10^{-12} s. This is the time range over which a pair of molecules after an encounter in a liquid, remains in proximity and either reacts or separates irreversibly.⁴ Detection of magnetic field effects may therefore provide information on pair processes in liquids involving doublet or triplet molecules. Magnetic field effects on radical reactions are closely related to the effects of nuclear spin and electron spin polarization.⁵ These effects are, in fact, based on the same physical mechanism.

Any realistic pair process involves an ensemble of molecular pairs with a certain distribution of magnetic interactions. This distribution results from random nuclear spin polarizations in doublets and random molecular orientations in case of triplets (see below). We have demonstrated earlier⁶ for processes between doublets, that this statistical aspect results in a simplification of the theoretical description. In this paper we will extend the previous analysis⁶ to

triplet molecules. The results on doublets will be reiterated here to demonstrate the close formal relationship to the triplet case.

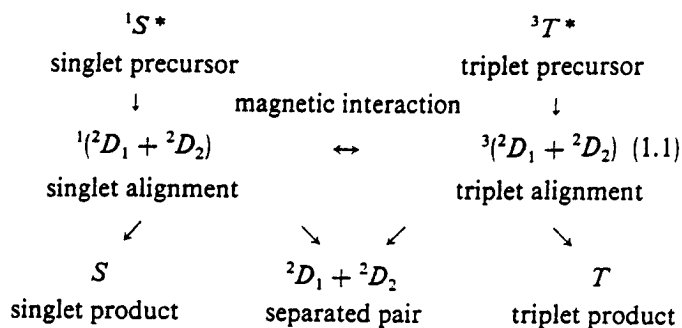
The spin dynamics of molecular ensembles with a distribution of interaction parameters is also of obvious interest as a model system for statistical mechanical behavior. One may ask whether an ensemble initially prepared in a pure quantum spin state will achieve an equilibrium between all degenerate states on account of the distribution of its random degrees of freedom. The answer which emerges from our investigation is that the asymptotic behavior of such ensembles depends very much on the degree of relaxation of the random degrees of freedom during the spin dynamics. In some instances equipartition among degenerate states is achieved asymptotically, in other instances only phase randomization is achieved. In cases of static ensembles, i.e., those with slow relaxation, a memory of the initial quantum state can persist for a long time. These phenomena are by no means novel. However, we feel that the spin dynamics of doublet and triplet molecules combines these facets of random behavior in an interesting way.

We will briefly summarize three sample bimolecular reactions to which we will then apply the theory.

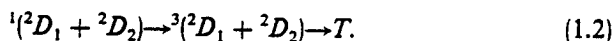
A. A doublet-doublet process

The first example involves doublet molecules (radicals) 2D_1 and 2D_2 . Such pairs can be generated thermally or photochemically and will be born in a pure two electron spin state, either singlet $^1(^2D_1 + ^2D_2)$ or triplet $^3(^2D_1 + ^2D_2)$. Since the recombination products also assume a singlet (S) or triplet (T) spin state the radical recombination is usually selective with respect to the spin alignments $^1(^2D_1 + ^2D_2)$ and

$^3(^2D_1 + ^2D_2)$. The overall reaction is schematically:



We want to consider the case that a radical pair born in a singlet alignment produces fast (ns) triplet products by means of magnetic interactions^{4,7,8}



The reaction depends on the probability $p_T(t)$ that the initial singlet pair assumes triplet character after time t before the end of the bimolecular encounter. The dominant magnetic interactions of organic doublet molecules are the Zeeman and the isotropic hyperfine interaction. These interactions are collected in the following spin Hamiltonian

$$H_{DD} = H_D^{(1)} + H_D^{(2)}, \quad (1.3)$$

$$H_D^{(i)} = \sum_k a_{ik} I_k^{(i)} \cdot S_i + g\mu_B \mathbf{B} \cdot S_i. \quad (1.4)$$

The sum in Eq. (1.4) extends over the nuclear spins $I_k^{(i)}$ of molecule i with hyperfine coupling constants a_{ik} and electron spin S_i , μ_B is the Bohr magneton of the electron, and \mathbf{B} the external magnetic field. We will assume identical g values for the doublet and triplet molecules considered here. A difference in the g values can give rise to additional effects at high fields which have been described for example in Ref. 9. The process monitored in any observation involves an ensemble of molecules with all possible initial nuclear spin orientations. The ensemble average can also include a stochastic dynamic situation in which electron spins visit several molecules and, thereby, randomly alter their nuclear spin environment.⁶ In Ref. 6 has been derived the approximate expression

$$p_T(t) = \langle \text{tr} Q_T(t) Q_S(0) \rangle, \quad (1.5)$$

where $\langle \rangle$ stands for the ensemble average over nuclear spin orientations (static ensemble) including a possible history of nuclear spin reorientations through random site visits (dynamic ensemble), tr denotes the trace over the electron spin states of the pair, and $Q_S(Q_T)$ denote the operators which project onto the singlet (triplet) subspaces

$$Q_S = \frac{1}{4} - S_1 \cdot S_2, \quad (1.6)$$

$$Q_T = \frac{3}{4} + S_1 \cdot S_2. \quad (1.7)$$

Evolution of the average gives

$$p_T(t) = \frac{3}{4} - {}_1U_2 \quad (1.8)$$

where ${}_1U$ describes the motion of the electron spin of the individual doublets

$${}_1U = \langle \text{tr} S_\alpha(t) S_\beta(0) \rangle. \quad (1.9)$$

The tensor product in the representation S_+ , S_- , and S_z of

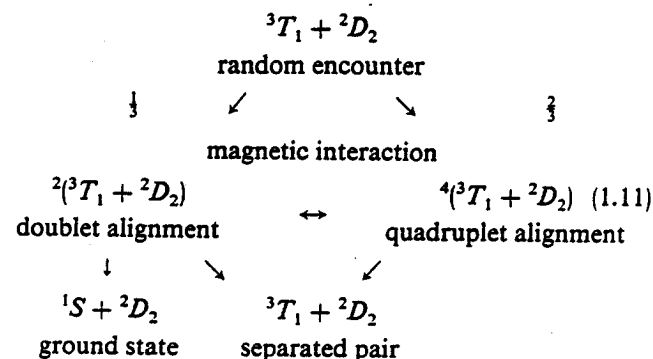
the electron spin operators is defined as

$$\begin{aligned}
 {}_1U_2 U = & \frac{1}{4} ({}_1U_{++} {}_2U_{--} + {}_1U_{+-} {}_2U_{-+} + {}_1U_{-+} {}_2U_{+-} \\
 & + {}_1U_{--} {}_2U_{++}) + \frac{1}{2} ({}_1U_{+z} {}_2U_{-z} + {}_1U_{-z} {}_2U_{+z} \\
 & + {}_1U_{z+} {}_2U_{z-} + {}_1U_{z-} {}_2U_{z+}) + {}_1U_{zz} {}_2U_{zz}. \quad (1.10)
 \end{aligned}$$

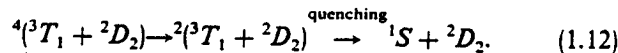
The evolution of the triplet probability of the pair has thereby been reduced to an evaluation of the ensemble averaged electron spin tensor ${}_1U$ for individual doublets. It has been demonstrated⁶ that the averaged spin motion yields a simple analytical description and a simple interpretation whereas the spin motion of individual doublet pairs require elaborate numerical calculations.⁸ We will show in this paper that the simplicity introduced by the ensemble average in the case of doublet pairs is also manifested by processes involving triplet molecules.

B. A triplet-doublet process

The second example we consider concerns triplet quenching by radicals and involves the encounter of a triplet molecule 3T_1 and a doublet 2D_2 . The encounter pair is either in a quadruplet ${}^4(^3T_1 + ^2D_2)$ or in a doublet ${}^2(^3T_1 + ^2D_2)$ overall spin state. The quenching process to the ground state ${}^1S_1 + ^2D_2$ which is of overall doublet character proceeds only from the doublet alignment ${}^2(^3T_1 + ^2D_2)$ and, hence, is selective with respect to the overall triplet-doublet spin state. The reaction scheme is



The reaction scheme involves the partitioning of a random encounter pair into a doublet and quadruplet alignment. The branching is determined statistically by the number of doublet substates (two) and the number of quadruplet substates (four). The fraction of pairs initially in a singlet state populates the ground state very fast. The remaining fraction of quadruplet pairs has to acquire doublet character by means of magnetic interactions before they can engage in the actual quenching process



The dominant magnetic interactions are the zero field splitting, i.e., the fine structure interaction of the triplet molecule, the hyperfine interaction of the doublet and the Zeeman interaction acting on both molecules. The interactions are collected in the following Hamiltonian

$$H_{TD} = H_T^{(1)} + H_D^{(2)}, \quad (1.13)$$

where $H_D^{(2)}$ is given by Eq. (1.4) and

$$H_T^{(1)} = D_1 S_{1z}^2 - E_1 (S_{1x}^2 - S_{1y}^2) + g\mu_B S_1 \cdot \mathbf{B}. \quad (1.14)$$

Here D_i and E_i are the zero field splitting constants and S_i is the electron spin operator in the molecular frame. In the laboratory frame rotated by the Eulerian angles $\Omega = (\phi, \theta, \psi)$ relative to the molecular frame the triplet Hamiltonian is¹⁰

$$H_{TL}^{(i)} = \frac{2}{3} D_i + \sum_{m,m'} h_m D_{m'm}^{(2)}(\Omega) T_{2m} + g\mu_B S_i \cdot B, \quad (1.15)$$

where $h_0 = \sqrt{3} D$, $h_{\pm 1} = 0$, $h_{\pm 2} = -E$, $D_{m'm}^{(2)}$ are the elements of the rotation matrix and T_{2m} second rank tensor operators.

Equation (1.15) shows that the triplet spin motion depends on the orientation of the molecule. The process (1.12) monitored in any observation involves an ensemble of pairs with all possible orientations of triplet molecules. The probability $p_D(t)$ for the transition within time t of the overall spin state of the pair from quadruplet to doublet, i.e., the probability relevant for process (1.12), has to be averaged over all orientations of the triplet molecule. Actually, in case that rotational diffusion plays a role on the time scale of the bimolecular reaction one also has to average over all stochastic reorientation processes. Another realization of orientational relaxation is triplet exciton migration in matrices of randomly oriented molecules. This situation may apply in the light harvesting systems of photosynthetic membranes.¹¹ However, in this case an anisotropic exciton interaction may also contribute to the spin dynamics.

The probability that an initial quadruplet pair assumes doublet character after time t can be written by analogy with Eq. (1.5)

$$p_D(t) = \frac{1}{4} \langle \text{tr} Q_D(t) Q_Q(0) \rangle. \quad (1.16)$$

$\langle \rangle$ denotes the average over the nuclear spin distribution of the doublet 2D_2 as well as the average over the orientations of 3T_1 . The average may include a history of relaxation processes for nuclear spin orientations or molecular orientations. tr denotes the trace over all electron spin states. Q_D and Q_Q are the projection operators onto the manifold of doublet and quadruplet pair states, respectively. One can derive

$$Q_D = \frac{1}{4} - \frac{3}{4} S_1 \cdot S_2, \quad (1.17)$$

$$Q_Q = \frac{3}{4} + \frac{3}{4} S_1 \cdot S_2. \quad (1.18)$$

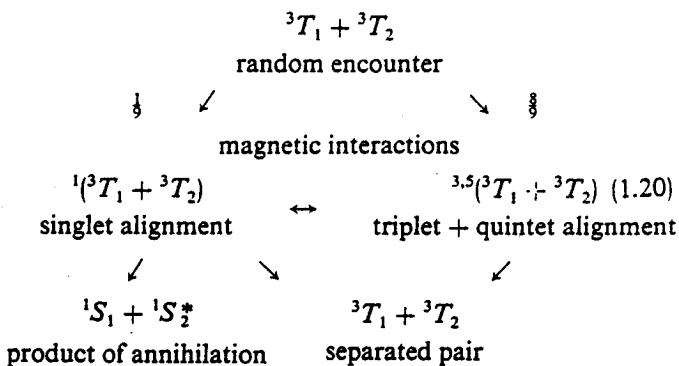
The prefactor $\frac{1}{4}$ in Eq. (1.16) takes account of the fact that there are four initial quadruplet states. The doublet probability can then be expressed again through the tensor operators in Eq. (1.9). With $\langle \text{tr} S_1 \cdot S_2 \rangle = 0$ one obtains

$$p_D(t) = \frac{1}{4} - \frac{1}{2} {}_1U_{:2}U. \quad (1.19)$$

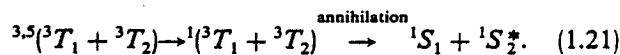
In this case U represents the spin correlation tensor of the triplet molecule 3T_1 and ${}_2U$ the spin correlation tensor of 2D_2 . The tensor product in Eq. (1.19) is as defined by Eq. (1.10).

C. A triplet-triplet process

Our third example concerns the triplet-triplet annihilation proceeding from the random encounter of two triplets 3T_1 and 3T_2 . The triplet pair is initially in either a singlet ${}^1({}^3T_1 + {}^3T_2)$ or a triplet ${}^3({}^3T_1 + {}^3T_2)$ or a quintet ${}^5({}^3T_1 + {}^3T_2)$ overall spin state with relative populations 1:3:5. The annihilation results in the product ${}^1S_1 + {}^1S_2^*$ with overall singlet character. Hence, the reaction route selects pairs in the ${}^1({}^3T_1 + {}^3T_2)$ singlet spin alignment. The scheme for the overall reaction is



The initial fraction $\frac{1}{4}$ of random encounter pairs in the singlet state proceeds very fast to the annihilation products. The remaining fraction $\frac{3}{4}$ of triplet and quintet pairs can annihilate only after change of the overall spin state



The spin motion is due to the interaction

$$H_{TT} = H_T^{(1)} + H_T^{(2)} \quad (1.22)$$

with $H_T^{(i)}$ as defined by Eq. (1.14). The process (1.21) is then governed by the probability $p_S(t)$ that the pairs initially in either a triplet or quintet state assume singlet character after time t :

$$p_S(t) = \frac{1}{4} \langle \text{tr} Q_S(t) Q_{T+Q}(0) \rangle. \quad (1.23)$$

In this case the average $\langle \rangle$ extends over all orientations of the triplet molecules 3T_1 and 3T_2 including again a possible history of random reorientations. The projection operators onto the singlet and (triplet + quintet) substates are, respectively,

$$Q_S = -\frac{1}{4} + \frac{1}{4} (S_1 \cdot S_2)^2, \quad (1.24)$$

$$Q_{T+Q} = \frac{3}{4} - \frac{1}{4} (S_1 \cdot S_2)^2. \quad (1.25)$$

With

$$\langle \text{tr} [S_1(t) \cdot S_2(t)]^2 \rangle = 12$$

one obtains

$$p_S(t) = \frac{1}{4} - \frac{1}{12} {}_1V_{::2}V. \quad (1.26)$$

The tensor product ${}_1V_{::2}V$ is defined by

$$\begin{aligned}
 {}_1V_{::2}V = & \frac{1}{16} ({}_1V_{+-zz} {}_2V_{-+zz} + {}_1V_{-+zz} {}_2V_{+-zz} + {}_1V_{zz+-} {}_2V_{-z-+} + {}_1V_{-z-+} {}_2V_{zz+-} + {}_1V_{zz-+} {}_2V_{+-zz} + {}_1V_{-z-+} {}_2V_{zz+-} \\
 & + {}_1V_{zz-+} {}_2V_{+-zz} + {}_1V_{z+z-} {}_2V_{-z-z+} + {}_1V_{-z-z+} {}_2V_{z+z-} + {}_1V_{z+-z} {}_2V_{-z-+} + {}_1V_{-z-+} {}_2V_{z+-z} + {}_1V_{z+-z} {}_2V_{-z-+} \\
 & + {}_1V_{-z-+} {}_2V_{z+-z}) + \frac{1}{16} ({}_1V_{++--} {}_2V_{--++} + {}_1V_{--++} {}_2V_{++--} + {}_1V_{+-+-} {}_2V_{-+--} + {}_1V_{-+--} {}_2V_{+-+-} \\
 & + {}_1V_{+-+-} {}_2V_{-+--} + {}_1V_{-+--} {}_2V_{+-+-} + {}_1V_{-+--} {}_2V_{+-+-}), \quad (1.27)
 \end{aligned}$$

where

$$V_{\alpha\beta\gamma\delta} = \langle \text{tr} S_\alpha(t) S_\beta(t) S_\gamma(0) S_\delta(0) \rangle \quad \alpha, \beta, \gamma, \delta = +, -, z.$$

In the following we will derive expressions for the tensorial elements for doublet and triplet molecules appearing in Eqs. (1.10) and (1.27). Section II considers spin dynamics of static ensembles without relaxation by paramagnetic-diamagnetic exchange or by rotational diffusion. Section III extends the description to dynamic ensembles in which such relaxation influences the spin dynamics.

II. SPIN CORRELATION TENSORS FOR STATIC ENSEMBLES

We have shown above for the three sample bimolecular processes (1.2), (1.12), and (1.21) that the relevant spin probabilities [see Eqs. (1.8), (1.19), and (1.26)] are determined by the elements of the spin correlation tensors for doublet and triplet molecules

$$U_{\alpha\beta}(t) = \langle \text{tr} S_\alpha(t) S_\beta(0) \rangle, \tag{2.1}$$

$$V_{\alpha\beta\gamma\delta}(t) = \langle \text{tr} S_\alpha(t) S_\beta(t) S_\gamma(0) S_\delta(0) \rangle. \tag{2.2}$$

The tensor elements (2.1) had been derived for doublet molecules in Ref. 6 in the approximation that the nuclear spin degrees of freedom are treated classically. This approximation applies as long as a large number of nuclear spins contributes to the hyperfine interaction in Eq. (1.4). The ensemble average which involves all orientations of the nuclear spins can then be carried out explicitly. The result in the case of *vanishing external magnetic fields* is

$$U_{\alpha\beta}(t) = {}^2c^{(0)}(t/\tau_i) \begin{cases} 1 & \text{for } \alpha\beta = + - \text{ or } - + \\ \frac{1}{2} & \text{for } \alpha\beta = zz, \\ 0 & \text{else} \end{cases} \tag{2.3a}$$

$${}^2c^{(0)}(x) = \frac{1}{2} [1 + 2 \exp(-x^2) - 4x^2 \exp(-x^2)]. \tag{2.3b}$$

In the case of *large external fields* such that the Zeeman interaction greatly exceeds the hyperfine interaction the *nonvanishing* elements of the spin correlation tensor are

$$U_{+-} = \exp(i\omega_0 t) {}^2C^{(0)}(t/\tau_i), \tag{2.4a}$$

$$U_{-+} = \exp(-i\omega_0 t) {}^2C^{(0)}(t/\tau_i), \tag{2.4b}$$

$$U_{zz} = \frac{1}{2}, \tag{2.4c}$$

$${}^2C^{(0)}(x) = \exp(-x^2). \tag{2.4d}$$

The time scale of the spin dynamics τ_i is related to the hyperfine coupling constants through

$$\tau_i^{-2} = \frac{1}{6} \sum_k a_{ik}^2 I_k^{(0)}(I_k^{(0)} + 1). \tag{2.5}$$

We want to derive now exact analytical expressions for the spin correlation tensors (2.1) and (2.2) describing triplet molecules. In this case the ensemble average is to be taken over all orientations of the molecules. We will again consider only the two limiting cases of weak and large external magnetic fields. In the zero field case the derivation of $U_{\alpha\beta}(t)$ and $V_{\alpha\beta\gamma\delta}(t)$ starts from the observation that the spin operators S_α and $S_\alpha S_\beta$ can be expressed by spherical tensor operators $T_{k\alpha}$ of rank $k = 0, 1, 2$. Representing S_α in the basis of triplet states $|1, \alpha\rangle (\alpha = 1, 0, -1)$ by the matrices

$$S_+ = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \quad S_- = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \quad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{2.6}$$

one can derive the following relationships:

$$S_z = -\sqrt{2} T_{10}, \quad S_\pm = \pm 2 T_{1\pm 1}, \tag{2.7}$$

$$S_z^2 = \frac{1}{\sqrt{3}} (\sqrt{2} T_{20} - T_{00}), \tag{2.8a}$$

$$S_z S_\pm = T_{1\pm 1} \mp T_{2\pm 1}, \tag{2.8b}$$

$$S_\pm S_z = -T_{1\pm 1} \mp T_{2\pm 1}, \tag{2.8c}$$

$$S_\pm^2 = 2 T_{2\pm 2}, \tag{2.8d}$$

$$S_+ S_- = -\frac{2}{\sqrt{6}} T_{20} - \frac{2}{\sqrt{3}} T_{00} - \sqrt{2} T_{10}, \tag{2.8e}$$

$$S_- S_+ = -\frac{2}{\sqrt{6}} T_{20} - \frac{2}{\sqrt{3}} T_{00} + \sqrt{2} T_{10}. \tag{2.8f}$$

In order to evaluate the expressions (2.1) and (2.2) one has to consider then the tensor operators $T_{k\alpha}$ in the Heisenberg picture

$$T_{k\alpha}(t) = \exp(iH_{TL}t/\hbar) T_{k\alpha} \exp(-iH_{TL}t/\hbar), \tag{2.9}$$

where H_{TL} denotes the triplet Hamiltonian in the *laboratory frame* as given by Eq. (1.15). This time-dependent operator can be evaluated in three steps: (1) transformation into the *molecular frame* according to

$$T_{k\alpha} = \sum_{\beta} D_{\beta\alpha}^{(k)}(\phi, \theta, \psi) \hat{T}_{k\beta}, \tag{2.10}$$

where $D_{\beta\alpha}^{(k)}(\phi, \theta, \psi)$ denotes the elements of the rotation matrix (see for example Ref. 10) and where $\hat{T}_{k\beta}$ denotes the operators defined in the *molecular frame*; (2) time development of $\hat{T}_{k\beta}$ in the Heisenberg picture and reexpansion in terms of tensor operators $\hat{T}_{l\gamma}$:

$$\exp(iH_T t/\hbar) \hat{T}_{k\beta} \exp(-iH_T t/\hbar) = \sum_{l\gamma} c_{l\gamma}^{k\beta}(t) \hat{T}_{l\gamma}; \tag{2.11}$$

(3) back transformation into the *laboratory frame* according to

$$\hat{T}_{l\gamma} = \sum_{\delta} D_{\delta\gamma}^{(l)}(-\psi, -\theta, -\phi) T_{l\delta}. \tag{2.12}$$

The overall expression for Eq. (2.9) is then

$$T_{k\alpha}(t) = \sum_{l, \beta, \gamma, \delta} D_{\delta\gamma}^{(l)}(-\psi, -\theta, -\phi) \times D_{\beta\alpha}^{(k)}(\phi, \theta, \psi) c_{l\gamma}^{k\beta}(t) T_{l\delta}. \tag{2.13}$$

This expression is most convenient for the ensemble average over all orientations ϕ, θ, ψ of the molecular frame. The average leads to the expressions

$$\langle D_{\delta\gamma}^{(l)}(-\psi, -\theta, -\phi) D_{\beta\alpha}^{(k)}(\phi, \theta, \psi) \rangle$$

which can be evaluated readily¹²

$$\langle D_{\delta\gamma}^{(l)}(-\psi, -\theta, -\phi) D_{\beta\alpha}^{(k)}(\phi, \theta, \psi) \rangle = \delta_{kl} \delta_{\beta\gamma} \delta_{\alpha\delta} \frac{1}{2l+1}. \tag{2.14}$$

One obtains

$$T_{k\alpha}(t) = {}^3c_k^{(0)}(t)T_{k\alpha}(0), \quad (2.15a)$$

where

$${}^3c_k^{(0)}(t) = \frac{1}{2k+1} \sum_{\beta=-k}^{+k} c_{k\beta}^{k\beta}(t). \quad (2.15b)$$

With

$$T_{00} = -\frac{2}{\sqrt{3}} \mathbf{1} \quad (2.16)$$

one can state immediately

$${}^3c_0^{(0)}(t) = 1. \quad (2.17)$$

The evaluation of ${}^3c_1^{(0)}(t)$ requires the functions $c_{1\beta}^{1\beta}(t)$ as defined in Eq. (2.11). The evolution operator is given by

$$U(t) = \exp(iH_T t / \hbar) = \begin{pmatrix} z & 0 & z' \\ 0 & 1 & 0 \\ z' & 0 & z \end{pmatrix}, \quad (2.18a)$$

where

$$z = \frac{1}{2} [\exp(i\omega_+ t) + \exp(i\omega_- t)], \quad (2.18b)$$

$$z' = \frac{1}{2} [\exp(i\omega_+ t) - \exp(i\omega_- t)], \quad (2.18c)$$

$$\omega_{\pm} = (D \pm E) / \hbar. \quad (2.18d)$$

One can then derive \hat{T}_{10} in the Heisenberg picture

$$U(t) \hat{T}_{10} \overline{U(t)} = \begin{pmatrix} |z|^2 - |z'|^2 & 0 & z \bar{z}' - z' \bar{z} \\ 0 & 0 & 0 \\ z \bar{z}' - z' \bar{z} & 0 & |z|^2 - |z'|^2 \end{pmatrix}.$$

This result implies

$$c_{10}^{10}(t) = |z|^2 - |z'|^2 = \cos(\omega_+ - \omega_-)t. \quad (2.19)$$

Similarly one determines

$$c_{1\beta}^{1\beta}(t) = \frac{1}{2} \cos \omega_+ t + \frac{1}{2} \cos \omega_- t, \quad \beta = \pm 1.$$

Equation (2.15b) provides then the correlation function

$${}^3c_1^{(0)}(t) = \frac{1}{3} \cos \omega_+ t + \frac{1}{3} \cos \omega_- t + \frac{1}{3} \cos(\omega_+ - \omega_-)t. \quad (2.20)$$

In order to evaluate ${}^3c_2^{(0)}(t)$ we consider the time development of $\hat{T}_{2\beta}$, i.e., $U(t) \hat{T}_{2\beta} \overline{U(t)}$, and obtain

$$c_{2\beta}^{2\beta}(t) = \begin{cases} 1, & \beta = 0 \\ \frac{1}{2} \cos \omega_+ t + \frac{1}{2} \cos \omega_- t, & \beta = 1. \\ \frac{1}{2} + \frac{1}{2} \cos(\omega_+ - \omega_-)t, & \beta = \pm 2. \end{cases} \quad (2.21)$$

This yields then the correlation function

$${}^3c_2^{(0)}(t) = \frac{2}{3} + \frac{1}{3} \cos \omega_+ t + \frac{1}{3} \cos \omega_- t + \frac{1}{3} \cos(\omega_+ - \omega_-)t. \quad (2.22)$$

This result shows that $\frac{2}{3}$ of the second rank tensor remains constant in time, while the remaining $\frac{1}{3}$ undergo oscillations. Equation (2.21) implies that the constant part of the correlation function originates from the fact that in the molecular frame T_{20} as well as half of $T_{2\pm 2}$ remains constant. This proves that the constant contribution to ${}^3c_2^{(0)}(t)$ originates from molecules in a certain orientation. If the molecules are subject to reorientations this constant contribution will be diminished successively with each reorientation event, following the geometric progression $2/5, 4/25, 16/125$, etc.

The time development of the tensors described by Eq. (2.15) together with the explicit spin correlation functions (2.17), (2.20), and (2.22) constitute a main result of this paper. These equations identify the three functions ${}^3c_k^{(0)}(t)$, which account for the spin motion of randomly oriented ensembles of triplet molecules.

The spin correlation tensors (2.1) and (2.2) can now be readily determined. From Eq. (2.7) follows for the vector operator $S(t)$ with components (2.6)

$$S(t) = {}^3c_1^{(0)}(t) S(0) \quad (2.23)$$

and, hence, for the elements of the spin correlation tensor

$$U_{\alpha\beta}(t) = {}^3c_1^{(0)}(t) \text{tr}(S_{\alpha} S_{\beta}), \quad (2.24)$$

where $\text{tr}(S_{\alpha} S_{\beta})$ has to be determined according to the definition (2.6). Similarly, the tensor elements $V_{\alpha\beta\gamma\delta}(t)$ are obtained by means of Eqs. (2.8), the inverse relationships

$$T_{20} = \frac{1}{\sqrt{6}} (3S_z^2 - 2), \quad (2.25a)$$

$$T_{2\pm 1} = \mp \frac{1}{2} (S_z S_{\pm} + S_{\pm} S_z), \quad (2.25b)$$

$$T_{2\pm 2} = \frac{1}{2} S_{\pm}^2, \quad (2.25c)$$

and Eqs. (2.7) and (2.16). For example, in case of $V_{z\gamma\delta}(t)$ one obtains from

$$\begin{aligned} S_z^2(t) &= \frac{1}{\sqrt{3}} [\sqrt{2} {}^3c_2^{(0)}(t) T_{20} - T_{00}] \\ &= \frac{1}{3} [{}^3c_2^{(0)}(t) (2S_z^2 - \frac{1}{2} S_+ S_- - \frac{1}{2} S_- S_+) + 2 \cdot 1] \end{aligned}$$

and, hence, by means of Eq. (2.6)

$$V_{z\gamma\delta}(t) = \text{tr} \begin{pmatrix} \frac{2}{3} + \frac{1}{3} {}^3c_2^{(0)}(t) & 0 & 0 \\ 0 & \frac{2}{3} - \frac{1}{3} {}^3c_2^{(0)}(t) & 0 \\ 0 & 0 & \frac{2}{3} + \frac{1}{3} {}^3c_2^{(0)}(t) \end{pmatrix} S_{\gamma} S_{\delta}. \quad (2.26)$$

This example shows that our algorithm for the spin correlation tensors (2.2) can be easily applied. The nonvanishing tensorial elements are found to be

$$V_{zzz} = \frac{4}{3} + \frac{2}{3} {}^3c_2^{(0)}, \quad (2.27a)$$

$$\begin{aligned} V_{z+-} = V_{z-+} = V_{+--} \\ = V_{-++} = \frac{2}{3} - \frac{2}{3} {}^3c_2^{(0)}, \end{aligned} \quad (2.27b)$$

$$\begin{aligned} V_{z+z-} = V_{z-z+} = V_{+z-z} \\ = V_{-z+z} = {}^3c_2^{(0)} - {}^3c_1^{(0)}, \end{aligned} \quad (2.27c)$$

$$\begin{aligned} V_{z+-z} = V_{z-+z} = V_{+zz-} \\ = V_{-zz+} = {}^3c_1^{(0)} + {}^3c_2^{(0)}, \end{aligned} \quad (2.27d)$$

$$V_{++++} = V_{----} = 4 {}^3c_2^{(0)}, \quad (2.27e)$$

$$V_{+ - - -} = V_{- - - +} = \frac{1}{2} + 2^3 c_1^{(0)} + \frac{1}{3}^3 c_2^{(0)}, \quad (2.27f)$$

$$V_{+ - - +} = V_{- - + -} = \frac{1}{2} - 2^3 c_1^{(0)} + \frac{1}{3}^3 c_2^{(0)}. \quad (2.27g)$$

We will consider now the case of large magnetic fields when the Zeeman interaction is dominant. In this limit the evolution operator in the laboratory frame

$$U_L(t) = \exp(iH_{TL}t/\hbar) \quad (2.28)$$

assumes a simple form since in the basis of triplet states $|1\alpha\rangle$ the Zeeman term in the Hamiltonian H_{TL} defined by Eq. (1.15) is diagonal and the weaker zero field splitting can only contribute to the diagonal. One derives

$$U_L(t) = \begin{pmatrix} \exp(i\Omega_1 t) & 0 & 0 \\ 0 & \exp(i\Omega_0 t) & 0 \\ 0 & 0 & \exp(i\Omega_{-1} t) \end{pmatrix}, \quad (2.29a)$$

where

$$\Omega_{\pm 1} = \omega_0 + (D/2\hbar)(1 + \cos^2 \theta) - (E/2\hbar) \sin^2 \theta \cos 2\psi, \quad (2.29b)$$

$$\Omega_0 = (D/\hbar)(1 - \cos^2 \theta) + (E/\hbar) \sin^2 \theta \cos 2\psi. \quad (2.29c)$$

$\omega_0 = g\mu_B B/\hbar$ is the Larmor frequency of a triplet and θ, ψ are two of the Eulerian angles. A straightforward calculation yields then the *nonvanishing* tensorial elements

$$U_{+-} = 4 \exp(i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.30a)$$

$$U_{-+} = 4 \exp(-i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.30b)$$

$$U_{zz} = 2, \quad (2.30c)$$

$$V_{zzz} = V_{zz+-} = V_{zz-+} = V_{+-zz} = V_{-+zz} = 2, \quad (2.31a)$$

$$V_{z+-z} = 2 \exp(i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.31b)$$

$$V_{+zz-} = 2 \exp(i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.31c)$$

$$V_{z-+z} = 2 \exp(-i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.31d)$$

$$V_{-zz+} = 2 \exp(-i\omega_0 t) \text{Re}\{^3C^{(0)}(t)\}, \quad (2.31e)$$

$$V_{++++} = 4 \exp(2i\omega_0 t), \quad (2.31f)$$

$$V_{--++} = 4 \exp(-2i\omega_0 t), \quad (2.31g)$$

$$V_{+---} = V_{-+--} = 8, \quad (2.31h)$$

$$V_{+--+} = V_{-++-} = 4, \quad (2.31i)$$

where

$$^3C^{(0)}(t) = \left\langle \exp \left[it \left(-\frac{D}{2\hbar} + \frac{3D}{2\hbar} \cos^2 \theta - \frac{3E}{2\hbar} \sin^2 \theta \cos 2\psi \right) \right] \right\rangle. \quad (2.32)$$

These expressions show that in the high field case a single correlation function accounts for the statistical aspects of the triplet spin motion. Only the tensor elements (2.30a), (2.30b), and (2.31b)–(2.31e) exhibit a decay of the spin phase, the remaining tensor elements are either completely coherent or constant. The reason for this conservation of the coherence properties of the spin correlation tensor is the symmetry of the Hamiltonian which endows the triplet states $|1\pm 1\rangle$ with identical phase factors.

The correlation function (2.32) can be further evaluated. The relationship

$$\frac{1}{2\pi} \int_0^{2\pi} d\psi \exp\left(-i \frac{3Et}{2\hbar} \sin^2 \theta \cos 2\psi\right) = J_0\left(\frac{3Et}{2\hbar} \sin^2 \theta\right)$$

yields the generalization of the Fresnel integral

$$\begin{aligned} ^3C^{(0)}(t) &= \exp(-iDt/2\hbar) \sqrt{3\pi Dt/4\hbar} \\ &\times \int_0^{\pi/2} d\theta \cos \theta \sin \theta J_0\left(\frac{3Et}{2\hbar} \sin^2 \theta\right) \\ &\times \left[J_{-1/2}\left(\frac{3Dt}{2\hbar} \cos^2 \theta\right) - i J_{1/2}\left(\frac{3Dt}{2\hbar} \cos^2 \theta\right) \right]. \end{aligned} \quad (2.33)$$

In the special case $E = 0$ an analytical expression can be derived

$$\begin{aligned} ^3C^{(0)}(t) &= \exp(-iDt/2\hbar) \sqrt{\pi\hbar/3Dt} \\ &\times \left[C\left(\sqrt{\frac{3Dt}{\pi\hbar}}\right) + iS\left(\sqrt{\frac{3Dt}{\pi\hbar}}\right) \right]. \end{aligned} \quad (2.34)$$

Here $C(z)$ and $S(z)$ denote the Fresnel integrals¹³

$$C(z) = \int_0^z dt \cos(\pi t^2/2), \quad S(z) = \int_0^z dt \sin(\pi t^2/2), \quad (2.35a)$$

which can be evaluated by virtue of

$$C(z) + iS(z) = \frac{1+i}{2} \{1 - \text{erfc}[(1-i)\sqrt{x/2}]\}. \quad (2.35b)$$

If one replaces D by the effective¹⁴ value

$$D^* = \sqrt{D^2 + 3E^2} \quad (2.36)$$

Eq. (2.34) together with the D value of Eq. (2.36) should provide a good approximation also in the case $E \neq 0$.

III. SPIN CORRELATION TENSORS FOR DYNAMIC ENSEMBLES

In case of dynamic ensembles one needs to average the correlation tensors (2.1) and (2.2) over the nuclear spin configurations (doublets), over the molecular orientations (triplets), as well as over the stochastic history of these properties. In case of doublets the nuclear spin configuration can be altered due to diamagnetic–paramagnetic exchange processes



whereupon an unpaired electron spin randomly visits several molecular sites. In case of triplet molecules the orientation can change due to rotational diffusion or triplet exciton migration in random matrices which induces a further randomization of the zero field splitting interaction.

The case of doublet molecules had been treated in Ref. 6 and is shortly reviewed here. The reaction process (3.1) alters the spin correlation tensor. At zero field the tensorial elements are

$$^iU_{\alpha\beta} = ^2c(t/\tau_i) \begin{cases} 1 & \text{for } \alpha\beta = +- \text{ or } -+ \\ \frac{1}{2} & \text{for } \alpha\beta = zz, \\ 0 & \text{else} \end{cases} \quad (3.2a)$$

where the correlation function $^2c^{(0)}(t/\tau_i)$ of Eq. (2.3) has been replaced by^{6,15}

$${}^2c(t) = \sum_{n=1}^{\infty} {}^2c^{(n)}(t). \quad (3.2b)$$

In this expansion ${}^2c^{(n)}(t)$ describes the contribution of $n - 1$ exchange events (3.1). In case of 1st order kinetics for the paramagnetic-diamagnetic exchange (3.1) with rate constant τ_e one has for $n > 1$:

$${}^2c^{(1)}(t) = {}^2c^{(0)}(t/\tau_e)\exp(-t/\tau_e), \quad (3.2c)$$

$${}^2c^{(n)}(t) = \frac{1}{\tau_e} \int_0^t dt' {}^2c^{(1)}(t-t')c^{(n-1)}(t'). \quad (3.2d)$$

Similarly, the tensorial elements for the high field case (2.4) are altered. In this case the correlation function ${}^2C^{(0)}(t/\tau_e)$ is replaced by ${}^2C(t)$, i.e.,

$$iU_{\alpha\beta}(t) = \begin{cases} \exp(i\omega_0 t) {}^2C(t) & \text{for } \alpha\beta = + - \\ \exp(-i\omega_0 t) {}^2C(t) & \text{for } \alpha\beta = - + \\ \frac{1}{2} & \text{for } \alpha\beta = zz \\ 0 & \text{else} \end{cases} \quad (3.3)$$

where ${}^2C(t)$ is to be determined in complete analogy to Eqs. (3.2b)–(3.2d).

The stochastic dynamics of an ensemble of triplet molecules involves rotational diffusion or triplet exciton migration. These processes can induce an orientational redistribution resulting in an orientational equipartition with a certain relaxation time τ_r . We will not describe the underlying dynamics in detail but rather assume a Poisson process of repeated reorientation events. Each reorientation event is supposed to induce complete orientational randomization. To implement this model we notice that in Sec. II the spin motion of triplet molecules in the low field situation is accounted for by three correlation functions ${}^3c_k^{(0)}(t)$ in Eq. (2.15). In the case of an ensemble undergoing stochastic reorientations these correlation functions have to be replaced by altered correlation functions ${}^3c_k(t)$ which are determined in analogy to Eqs. (3.2b)–(3.2d), i.e.,

$${}^3c_k(t) = \sum_{n=1}^{\infty} {}^3c_k^{(n)}(t), \quad (3.4a)$$

where for $n > 1$:

$${}^3c_k^{(1)}(t) = {}^3c_k^{(0)}(t)\exp(-t/\tau_r), \quad (3.4b)$$

$${}^3c_k^{(n)}(t) = \frac{1}{\tau_r} \int_0^t dt' {}^3c_k^{(1)}(t-t')c_k^{(n-1)}(t'). \quad (3.4c)$$

The dynamics of the spin tensor operators is then described by

$$T_{k\alpha}(t) = {}^3c_k(t)T_{k\alpha}(0), \quad k = 0, 1, 2. \quad (3.4d)$$

An identical construction of the dynamically altered correlation functions applies to the high field situation.

The evaluation of the correlation functions

$$g(t) = {}^2c(t), {}^2C(t), {}^3c_k(t), {}^3C(t) \quad (3.5)$$

is most simple for the Laplace transformed functions

$$\hat{g}(s) = \int_0^{\infty} dt \exp(-st)g(t). \quad (3.6a)$$

One can show that $\hat{g}(s)$ complying to Eqs. (3.2b)–(3.2d) must satisfy⁶

$$\hat{g}(s) = \hat{g}^{(0)}(s + \tau^{-1})/[1 - \tau^{-1}\hat{g}^{(0)}(s + \tau^{-1})], \quad (3.6b)$$

where $\hat{g}^{(0)}(s)$ is the Laplace transform of the relevant correlation functions of the static ensemble and $\tau = \tau_e$ or $\tau = \tau_r$. For ${}^3c_0^{(0)}(t) = 1$, i.e., $\hat{g}^{(0)}(s) = 1/s$, a straightforward calculation yields

$${}^3c_0(t) = 1, \quad (3.7)$$

a result which is of course to be expected. In case of very large τ , i.e., for a relaxation process slow on the time scale of the spin motion, the approximation 1st order in τ^{-1} is

$$\hat{g}(s) \simeq \hat{g}^{(0)}(s + \tau^{-1}) + \tau^{-1}\hat{g}^{(0)}(s + \tau^{-1})\hat{g}^{(0)}(s). \quad (3.8a)$$

Back transformation yields

$$g(t) \simeq \exp(-t/\tau)\hat{g}^{(0)}(t) + \tau^{-1} \times \int_0^t dt' \exp(-t'/\tau)\hat{g}^{(0)}(t')\hat{g}^{(0)}(t-t'). \quad (3.8b)$$

This approximation applies only for times $t \lesssim \tau$. For longer times one needs to extend this approximation to account for 2, 3, ... stochastic events.

In the limit of fast relaxation processes, i.e., $\tau = \tau_e, \tau_r$ small compared to the time scale of the spin motion, $g(t)$ decays exponentially. The approximate expression which correctly reproduces $g(0)$ and $\dot{g}(0)$ is¹⁶

$$g(t) \simeq \exp[-t/\hat{g}(0)]. \quad (3.9a)$$

In the limit considered $\hat{g}(0)$, i.e.,

$$\hat{g}(0) = \hat{g}^{(0)}(\tau^{-1})/[1 - \tau^{-1}\hat{g}^{(0)}(\tau^{-1})] \quad (3.9b)$$

depends only on the short-time behavior of $g^{(0)}(t)$. As $g^{(0)}(t)$ characterizes a coherent quantum process, the first derivative at $t = 0$ vanishes and, therefore,

$$\hat{g}^{(0)}(t) \simeq 1 + \frac{1}{2}\ddot{g}^{(0)}(0)t^2. \quad (3.9c)$$

From this results the high frequency behavior of the Laplace transform

$$\hat{g}^{(0)}(\tau^{-1}) \simeq \tau + \tau^3\ddot{g}^{(0)}(0) \quad (3.9d)$$

and, hence,

$$\hat{g}(0) \simeq -[\tau\ddot{g}^{(0)}(0)]^{-1}. \quad (3.9e)$$

The experimental investigation of doublet spin dynamics under the circumstances of diamagnetic-paramagnetic exchange in liquids revealed¹⁷ that τ_e is very long compared to the time scale of the spin dynamics of most doublets and, hence, one can expect that approximation (3.8) will apply. For doublet processes involving electron transfer at semiconductor surfaces¹⁸ the diamagnetic-paramagnetic exchange corresponds to the electron or hole conduction and then should be much faster than the spin motion such that Eq. (3.9) applies. In this latter case one determines for the spin correlation function for doublets at *low fields*

$${}^2c(t/\tau_e) = \exp(-4t\tau_e/\tau_e^2) \quad (3.10)$$

and at *high fields*

$${}^2C(t/\tau_e) = \exp(-2t\tau_e/\tau_e^2). \quad (3.11)$$

For triplet processes the spin motion is expected to proceed on a time scale of 100 to 1 ps or shorter. Rotational diffusion may be slower, e.g., in viscous media and at lower temperatures, but more likely will be faster in many circumstances. In this case Eqs. (3.9) apply again. For the *low field* correlation functions one determines from Eqs. (2.20) and

(2.22) employing Eq. (3.9e)

$${}^3\hat{c}_1(0) = 3/2(\omega_+^2 + \omega_-^2 - \omega_+\omega_-)\tau_r,$$

$${}^3\hat{c}_2(0) = 5/2(\omega_+^2 + \omega_-^2 - \omega_+\omega_-)\tau_r,$$

from which follows according to Eq. (3.9a)

$${}^3c_1(t) = \exp[-2t\tau_r(\omega_+^2 + \omega_-^2 - \omega_+\omega_-)/3], \quad (3.12)$$

$${}^3c_2(t) = \exp[-2t\tau_r(\omega_+^2 + \omega_-^2 - \omega_+\omega_-)/5]. \quad (3.13)$$

For a derivation of the *high field* correlation function ${}^3C(t)$ we note that Eq. (2.32) has the short time expansion

$${}^3C^{(0)}(t) \simeq 1 + \frac{1}{2}t^2 {}^3\ddot{C}^{(0)}(0), \quad (3.14a)$$

where

$${}^3\ddot{C}^{(0)}(0) = - \left\langle \left[\frac{3D}{2\hbar} \left(\cos^2 \theta - \frac{1}{3} \right) - \frac{3E}{2\hbar} \sin^2 \theta \cos 2\psi \right] \right\rangle.$$

The average over θ, ψ with the definition Eq. (2.36) of D^* yields

$${}^3\ddot{C}^{(0)}(0) = -4 \left(\frac{3D^*}{2\hbar} \right)^2 / 45$$

and, hence,

$${}^3C(t) = \exp \left[-4t\tau_r \left(\frac{3D^*}{2\hbar} \right)^2 / 45 \right]. \quad (3.15)$$

IV. SPIN PAIR DYNAMICS

In the following we present the ensemble averaged spin pair probabilities for the three sample processes introduced in Sec. I. By means of the spin correlation tensors derived in Secs. II and III it is a simple matter to evaluate these probabilities.

A. The doublet-doublet process

$${}^1({}^2D_1 + {}^2D_2) \rightarrow {}^3({}^2D_1 + {}^2D_2)$$

We consider first the triplet probability $p_T(t)$ of a pair of doublets in a static ensemble generated at $t = 0$ in a singlet state. This probability can be evaluated by means of Eqs. (1.8) and (1.10). In the case of *low magnetic fields* when the Zeeman energy is small compared to the hyperfine interaction energy in either molecule

$$g\mu_B B / \hbar \ll \tau_1^{-1}, \tau_2^{-1} \quad (4.1a)$$

the tensors U are given by Eq. (2.3a) and one obtains

$$p_T(t) = \frac{2}{3} - \frac{2}{3} {}^2c^{(0)}(t/\tau_1) {}^2c^{(0)}(t/\tau_2). \quad (4.1b)$$

The correlation function ${}^2c^{(0)}(t)$ is provided by Eq. (2.3b) and the time constants τ_i are determined by the hyperfine coupling constants through Eq. (2.5). At *intermediate fields*

$$\tau_2^{-1} \ll g\mu_B B / \hbar \ll \tau_1^{-1} \quad (4.2a)$$

one can apply Eqs. (2.3) for 2D_1 and the high field expressions (2.4) for 2D_2 . The resulting spin probability is

$$p_T(t) = \frac{2}{3} - \frac{1}{3} {}^2c^{(0)}(t/\tau_1) - \frac{1}{3} {}^2c^{(0)}(t/\tau_1) {}^2C^{(0)}(t/\tau_2) \cos(g\mu_B B t / \hbar). \quad (4.2b)$$

At *high fields*

$$\tau_1^{-1}, \tau_2^{-1} \ll g\mu_B B / \hbar \quad (4.3a)$$

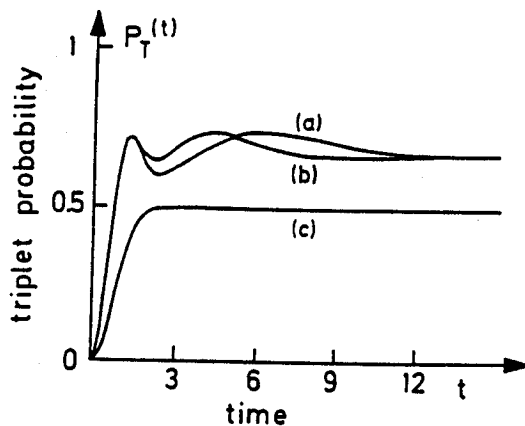


FIG. 1. Triplet probability of doublet-doublet encounter pairs starting in a singlet state $\tau_1 = 1, \tau_2 = 5$, (a) at zero external field, evaluated according to Eq. (4.1), (b) at intermediate magnetic fields with $g\mu_B B / \hbar = 3/\tau_2$, evaluated according to Eq. (4.2); (c) at high magnetic fields, evaluated according to Eq. (4.3).

Eq. (2.4) apply for both radicals and the triplet probability is

$$p_T(t) = \frac{1}{2} - \frac{1}{2} {}^2C^{(0)}(t/\tau_1) {}^2C^{(0)}(t/\tau_2). \quad (4.3b)$$

The time development of the triplet probabilities for the field situations (4.1a), (4.2a), and (4.3a) is shown in Fig. 1. The diagram reveals the following asymptotic behavior for the static ensemble at $t \rightarrow \infty$:

$$p_T(t) \sim \frac{2}{3} \quad (\text{low fields and intermediate fields}) \quad (4.4a)$$

$$p_T(t) \sim \frac{1}{2} \quad (\text{high fields}).$$

This behavior results from the asymptotic values of the correlation functions

$$\lim_{x \rightarrow \infty} {}^2c^{(0)}(x) = \frac{1}{3}, \quad (4.4b)$$

$$\lim_{x \rightarrow \infty} {}^2C^{(0)}(x) = 0.$$

The fact that ${}^2c^{(0)}(x)$ does not vanish asymptotically implies that despite the ensemble average there is some indefinite 'memory' of the initial state. The reason for this behavior is that (in case of large numbers of nuclear spins, the case considered here) the hyperfine coupling at low fields preserves the electron spin polarization along the direction of $\sum_k a_{ik} \mathbf{I}_k^{(i)}$ in each doublet while it averages out the other two directions, i.e., $\frac{1}{3}$ of the polarization is conserved.

This behavior is being altered when a doublet undergoes diamagnetic-paramagnetic exchange whereupon the nuclear spin orientations are randomized and, as a result, no spin component is conserved anymore. We consider first the case when the diamagnetic-paramagnetic exchange is slow. To describe this situation one has to replace the correlation functions ${}^2c^{(0)}(x)$ and ${}^2C^{(0)}(x)$ in (4.1b), (4.2b), and (4.3b) by the correlation functions ${}^2c(x)$ and ${}^2C(x)$ introduced in Sec. III. In the case of slow exchange the correlation functions are then given by Eq. (3.8). Figure 2 compares the resulting time development of $p_T(t)$ to the situation of no exchange. One observes that the exchange process increases the asymptotic value of the low field triplet probability to values above $\frac{2}{3}$,

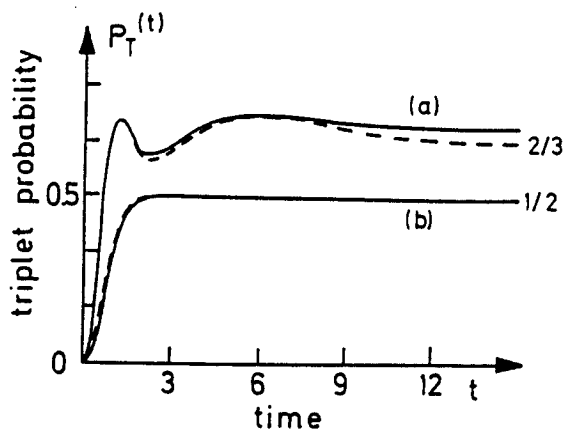


FIG. 2. Comparison between the triplet probability of a doublet-doublet pair ${}^2D_1 + {}^2D_2$ as in Fig. 1 (---) and the triplet probability of such pair which undergoes diamagnetic-paramagnetic exchange ${}^2D_1 + {}^1M_1 \rightarrow {}^1M_1 + {}^2D_1$ with a relaxation time $\tau_e = 10$ (—); the correlation functions ${}^2c(t)$ and ${}^2C(t)$ of 2D_1 had been determined according to Eq. (3.8), (a) zero field situation, (b) high field situation.

whereas the high field probability is only little affected. One can prove that the exact correlation functions in case of exchange both vanish asymptotically

$$\lim_{x \rightarrow \infty} {}^2c(x) = 0, \quad (4.5a)$$

$$\lim_{x \rightarrow \infty} {}^2C(x) = 0.$$

From this results the behavior of the triplet probabilities at $t \rightarrow \infty$:

$$p_T(t) \sim \frac{3}{4} \text{ (low fields)}, \quad p_T(t) \sim \frac{1}{2} \text{ (high fields)}. \quad (4.5b)$$

This asymptotic behavior manifests itself most clearly in the limit of fast exchange. In this case one needs to replace the correlation functions ${}^2c^{(0)}(x)$ and ${}^2C^{(0)}(x)$ by their dynamic counterparts as given by Eqs. (3.10) and (3.11), respectively. The resulting time development of the triplet probabilities is presented in Fig. 3. The triplet probability at low fields assumes its asymptotic value fast whereas the approach of the high field triplet probability to its asymptotic value $\frac{1}{2}$ is slowed down. The influence of diamagnetic-paramagnetic exchange processes on the dynamics of doublets has been

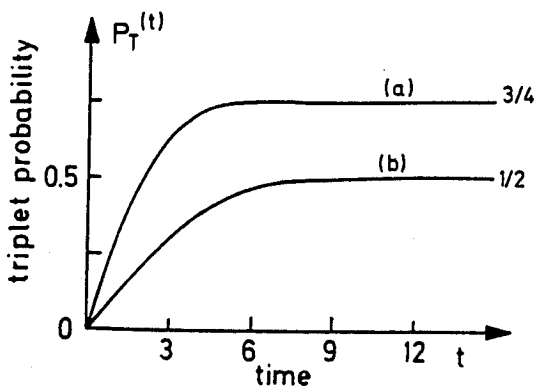


FIG. 3. Triplet probability as in Fig. 1, but for a pair undergoing fast diamagnetic-paramagnetic exchange ${}^2D_1 + {}^1M_1 \rightarrow {}^1M_1 + {}^2D_1$ with $\tau_e = 0.1$; the correlation functions ${}^2c(t)$ and ${}^2C(t)$ of 2D_1 had been determined according to Eqs. (3.10) and (3.11), (a) zero field situation, (b) high field situation.

demonstrated here only for the limiting cases of low and high fields. This influence is actually even more pronounced at intermediate fields⁶ and opened the possibility to monitor exchange processes (3.1) by an analysis of the magnetic field dependence.¹⁷

The asymptotic values (4.5b) of $p_T(t)$ can be explained by simple statistical models. In the low field situation all four states of the doublet spin pair without hyperfine coupling, i.e., the states S_0 (singlet) and T_{+1}, T_0, T_{-1} (triplet) are degenerate. The hyperfine coupling brings about a 'mixing' of these states, such that the initial population of S_0 develops into an equipartition of all four states. This model predicts then the fraction of $\frac{3}{4}$ of triplet character in agreement with the exact result (4.5b).

The high field behavior of $p_T(t)$ could also be explained as an equilibrium among the degenerate states S_0 and T_0 of a doublet pair without hyperfine coupling. However, this explanation is not in harmony with the actual spin dynamics and fails when applied to doublet-triplet processes. The correct explanation invokes phase randomization rather than equipartition between degenerate states. One considers the wave functions of the degenerate S_0 and T_0 states which in the basis of doublet product states

$$|1\rangle = |\frac{1}{2}\frac{1}{2}\rangle|\frac{1}{2} - \frac{1}{2}\rangle$$

and

$$|2\rangle = |\frac{1}{2} - \frac{1}{2}\rangle|\frac{1}{2}\frac{1}{2}\rangle$$

are

$$|S_0\rangle = (|1\rangle - |2\rangle)/\sqrt{2}, \quad |T_0\rangle = (|1\rangle + |2\rangle)/\sqrt{2}.$$

Phase randomization of the initial state $|S_0\rangle$ implies the transition

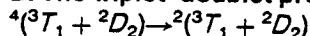
$$|S_0\rangle \rightarrow (\exp(i\phi_1)|1\rangle - \exp(i\phi_2)|2\rangle)/\sqrt{2} = \exp(i\phi_1)|S_0(\phi_2 - \phi_1)\rangle,$$

where the phase difference $\phi_2 - \phi_1$ is random. The resulting triplet probability is then for a particular $\phi = \phi_2 - \phi_1$:

$$|\langle T_0|S_0(\phi)\rangle|^2 = \frac{1}{2}(1 + \cos \phi).$$

Average over all phase angles $0 \leq \phi < 2\pi$ yields then the correct asymptotic value $\frac{1}{2}$.

B. The triplet-doublet process



We consider now the probability $p_D(t)$ for the process ${}^4({}^3T_1 + {}^2D_2) \rightarrow {}^2({}^3T_1 + {}^2D_2)$ from which a magnetic field dependence of the quenching of triplets by radicals can originate.² This probability can be determined from Eqs. (1.19) and (1.10). In the case of low magnetic fields, i.e., Zeeman interactions small compared to the zero field splitting as well as to the hyperfine coupling, the spin correlation tensors are given by Eqs. (2.3a) and (2.24). The resulting *low field* probability is

$$p_D(t) = \frac{1}{3} - \frac{1}{3} {}^3c_1^{(0)}(t) {}^2c^{(0)}(t/\tau_2), \quad (4.6)$$

where the correlation functions ${}^2c^{(0)}(x)$ and ${}^3c_1^{(0)}(t)$ are given by Eqs. (2.3b) and (2.20), respectively. At high fields the spin correlation tensors of Eqs. (2.4a) and (2.30) have to be employed. This yields the *high field* probability

$$p_D(t) = \frac{1}{3} - \frac{1}{3} \text{Re} [{}^3C^{(0)}(t)] {}^2C^{(0)}(t/\tau_2), \quad (4.7)$$

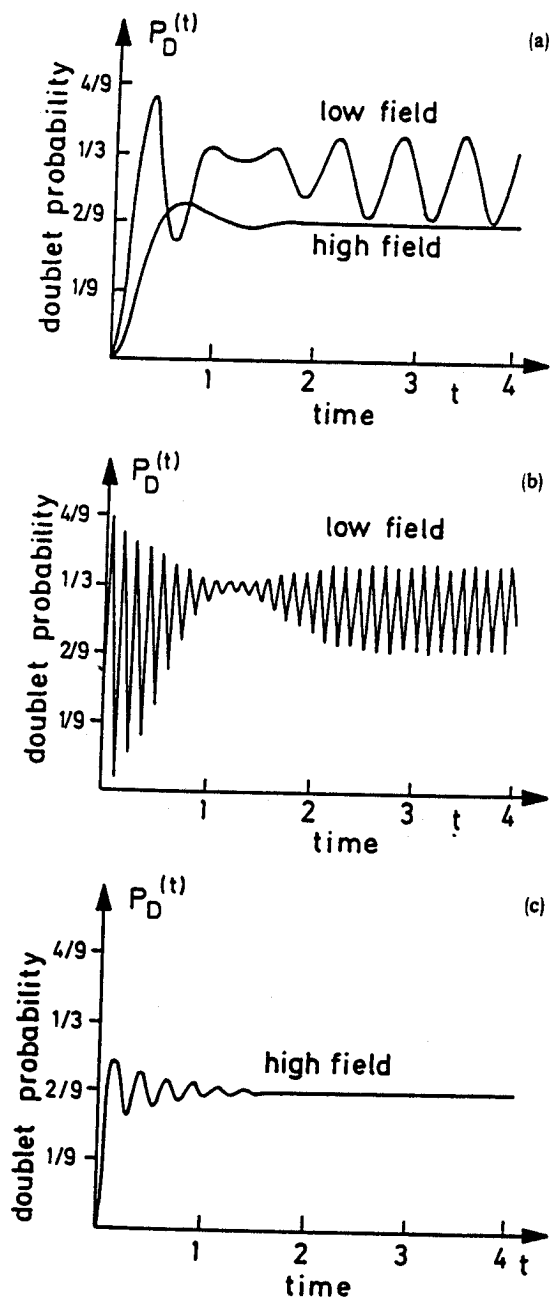


FIG. 4. Doublet probability of a doublet-triplet encounter pair starting in a quadruplet electron spin state for a low and a high field situation evaluated according to Eqs. (4.6) and (4.7), respectively, (a) $\tau_1 = 1$, $\tau_2 = \hbar/\sqrt{D^2 + 3E^2} = 0.1$, (b) $\tau_1 = 1$, (c) $\tau_2 = 0.02$.

where ${}^2C^{(0)}(x)$ and ${}^3C^{(0)}(t)$ are given by Eqs. (2.4d) and Eqs. (2.32)–(2.36), respectively.

The time development of $p_D(t)$ is illustrated in Fig. 4. Figure 4(a) shows a situation when the zero field splitting in 3T_1 and the hyperfine coupling in 2D_2 are of similar strength. The low field probability asymptotically oscillates around a value $\frac{1}{3}$, again above the asymptotic high field probability $\frac{2}{9}$, a value which is approached after a few strongly damped oscillations. Figures 4(b) and 4(c) show a situation when the zero field splitting in 3T_1 is much stronger than the hyperfine coupling in 2D_2 , a situation which should prevail most often. The oscillations of $p_D(t)$ exhibit a shorter period in this case, else the behavior of $p_D(t)$ is not altered compared to the situation of Fig. 4(a).

In the low field case the correlation function for $E = 0$ is

$${}^3c_1^{(0)}(t) = \frac{1}{3}[1 + \cos(Dt/\hbar)],$$

i.e., $E = 0$ introduces a constant contribution $\frac{1}{3}$ and the asymptotic behavior of $p_D(t)$ is

$$p_D(t) \sim \frac{2}{9} - \frac{1}{9} \cos(Dt/\hbar).$$

Hence, in the particular instance of vanishing E as presented in Fig. 4 the asymptotic oscillations appear around the value $\frac{2}{9}$. The general average value, however, is $\frac{1}{3}$. This value can be explained again by an equipartition among the degenerate overall spin states of the triplet-doublet pair (neglecting the zero field splitting and the hyperfine coupling interactions) ${}^4Q_m, m = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ (quadruplet) and $D_m, m = -\frac{1}{2}, \frac{1}{2}$ (doublet). The magnetic interactions neglected induce a mixing of the initially occupied quadruplet states with the doublet states. Equipartition implies that $\frac{1}{3}$ doublet character is reached asymptotically. The fact, that $p_D(t)$ exhibits asymptotic oscillations implies an indefinite 'phase memory' of the initial state.

In the case of high fields only two of the quadruplet states are degenerate with the doublet states, i.e., ${}^4Q_{-1/2}$ with $D_{-1/2}$ and ${}^4Q_{1/2}$ with $D_{1/2}$. The asymptotic value of $p_D(t)$ in this case can be explained as resulting from phase randomization. Considering the states ${}^4Q_{1/2}$ and $D_{1/2}$ which in the basis of triplet and doublet product states

$$|1\rangle = |10\rangle|\frac{1}{2}\frac{1}{2}\rangle$$

and

$$|2\rangle = |11\rangle|\frac{1}{2}-\frac{1}{2}\rangle$$

are

$$|{}^4Q_{1/2}\rangle = \sqrt{2/3}|1\rangle + \sqrt{1/3}|2\rangle,$$

$$|D_{1/2}\rangle = -\sqrt{1/3}|1\rangle + \sqrt{2/3}|2\rangle,$$

the magnetic interactions induce a phase for the initial state

$$|{}^4Q_{1/2}\rangle \rightarrow |{}^4Q_{1/2}(\phi)\rangle = \sqrt{2/3}|1\rangle + \sqrt{1/3} \exp(i\phi)|2\rangle.$$

This state assumes thereby the doublet character

$$|\langle D_{1/2} | {}^4Q_{1/2}(\phi) \rangle|^2 = \frac{1}{3}(1 - \cos \phi).$$

Phase randomization results in the asymptotic value $\frac{2}{9}$. However, since only half of the initially populated quadruplet states couple with the doublet states in this way, the asymptotic value of $p_D(t)$ should be $\frac{1}{3}$, in agreement with the exact value.

In case that the doublets undergo paramagnetic-diamagnetic exchange or the triplets are being reoriented randomly one needs to replace the correlation functions ${}^2c^{(0)}$, ${}^2C^{(0)}$, ${}^3c_1^{(0)}$, and ${}^3C^{(0)}$ by their dynamic counterparts as detailed in Sec. III. In case of fast exchange one replaces ${}^2c^{(0)}$ by 2c of Eq. (3.10) and ${}^2C^{(0)}$ by 2C of Eq. (3.11). In case of fast orientational relaxation one replaces ${}^3c_1^{(0)}$ by 3c_1 of Eq. (3.12) and ${}^3C^{(0)}$ by 3C of Eq. (3.15). The resulting doublet probabilities are presented in Fig. 5. This figure demonstrates that the relaxation processes damp the oscillatory behavior of $p_D(t)$ in the low field case and, thereby, lead to a constant asymptotic value $\frac{1}{3}$.

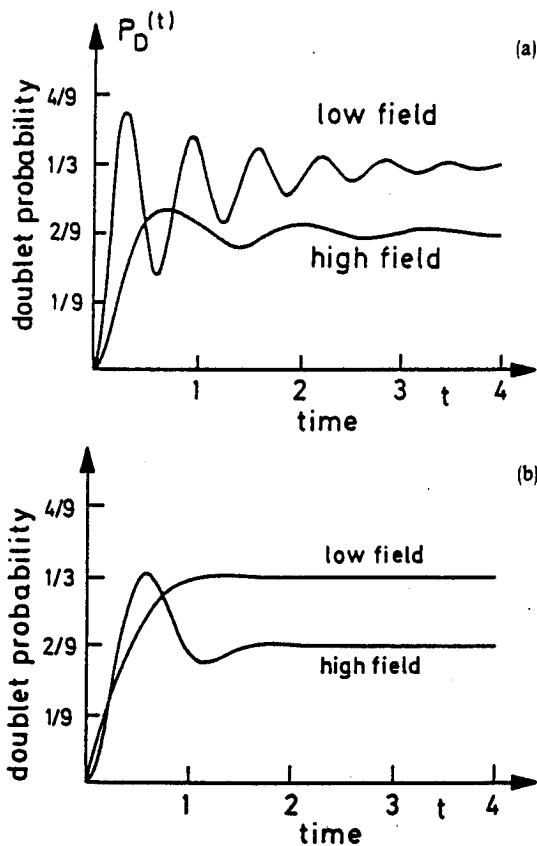


FIG. 5. Doublet probability as in Fig. 4(a), but for dynamic ensembles, (a) ensemble undergoing diamagnetic-paramagnetic exchange ${}^3D_2 + {}^1M_2 \rightarrow {}^1M_2 + {}^3D_2$; with $\tau_r = 0.25$, the correlation functions were determined as in Fig. 3, (b) ensemble undergoing orientational relaxation with $\tau_r = 0.025$, the correlation functions ${}^3c_1(t)$ and ${}^3C(t)$ were determined according to Eqs. (3.12) and (3.15), respectively.

C. The triplet-triplet process ${}^{3,5}({}^3T_1 + {}^3T_2) \rightarrow {}^1({}^3T_1 + {}^3T_2)$

We consider now the spin dynamics of the transition ${}^{3,5}({}^3T_1 + {}^3T_2) \rightarrow {}^1({}^3T_1 + {}^3T_2)$ which governs the magnetic field dependence of triplet-triplet annihilation.³ The singlet probability has to be evaluated from Eqs. (1.26) and (1.27). The spin correlation tensors for the low field situation are given by Eq. (2.27). One obtains for the *low field* singlet probability

$$p_S(t) = \frac{1}{3} - \frac{1}{24} {}^3c_1^{(0)}(t) {}^3\hat{c}_1^{(0)}(t) - \frac{5}{72} {}^3c_2^{(0)}(t) {}^3\hat{c}_2^{(0)}(t), \quad (4.8)$$

where the correlation functions ${}^3c_k^{(0)}$ and ${}^3\hat{c}_k^{(0)}$ for triplet 3T_1 and 3T_2 , respectively, are given by Eqs. (2.20) and (2.22). For high field situations the spin correlation tensors of Eq. (2.31) have to be employed. The resulting singlet probability at *high fields* is

$$p_S(t) = \frac{1}{18} - \frac{1}{18} \text{Re} [{}^3C^{(0)}(t) {}^3\hat{C}^{(0)}(t)], \quad (4.9)$$

where the correlation functions are given by Eq. (2.32).

The time development of the singlet probability is presented in Fig. 6 for the case $E = 0$ and $E \neq 0$. The probability exhibits oscillatory behavior which continues into the asymptotic region. The convergence to a constant value in Fig. 6(b) is only accidental since $p_S(t)$ resumes oscillations at later times. This becomes evident from an inspection of the

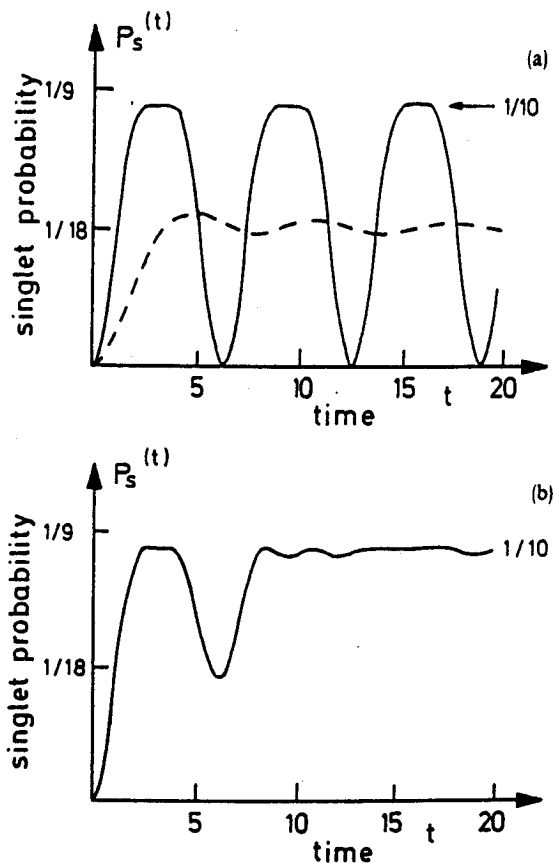


FIG. 6. Singlet probability of a triplet-triplet encounter pair starting in either a triplet or a quintet overall spin state at zero (—) and high (---) external magnetic field evaluated according to Eqs. (4.8) and (4.9), respectively, (a) $\tau_1 = \tau_2 = 1$, $\tau_i = \hbar/D$, $E = 0$, (b) same as (a) but with $\tau_i = \hbar/D^*$ and $E = D/10$.

functional forms of ${}^3c_k^{(0)}(t)$ in Eqs. (2.20) and (2.22). The maximum values which $p_S(t)$ reaches in the low field case are about $1/10$. This value derives from the fact that ${}^3c_2^{(0)}(t)$ entails the constant contribution $\frac{1}{3}$. Representation of ${}^3c_2^{(0)}(t)$ in the form

$${}^3c_2^{(0)}(t) = \frac{1}{3} + \frac{1}{3} {}^3c_1^{(0)}(t)$$

leads to the following separation of $p_S(t)$ in a constant and an oscillatory contribution

$$p_S(t) = \frac{1}{10} - \frac{1}{60} {}^3c_1^{(0)}(t) - \frac{1}{18} {}^3c_1^{(0)}(t) {}^3\hat{c}_1^{(0)}(t).$$

The high field probability does converge to a constant asymptotic value, i.e., $\frac{1}{18}$, albeit slowly since the convergence according to Eq. (2.34) goes as t^{-1} [the asymptotic values of the Fresnel integrals $C(z)$ and $S(z)$ both are $\frac{1}{2}$].

If one wishes to describe triplets which undergo orientational relaxation one needs to replace the correlation functions ${}^3c_k^{(0)}$ and ${}^3C^{(0)}$ in Eqs. (4.8) and Eq. (4.9), respectively, by their dynamic counterparts. In case of fast relaxation the expressions (3.12), (3.13), and (3.15) apply. The resulting singlet probabilities are presented in Fig. 7. The relaxation process produces the behavior that the constant asymptotic values $\frac{1}{3}$ and $\frac{1}{18}$ are quickly approached.

The asymptotic value $\frac{1}{3}$ of the low field situation can again be explained by the assumption that the spin dynamics

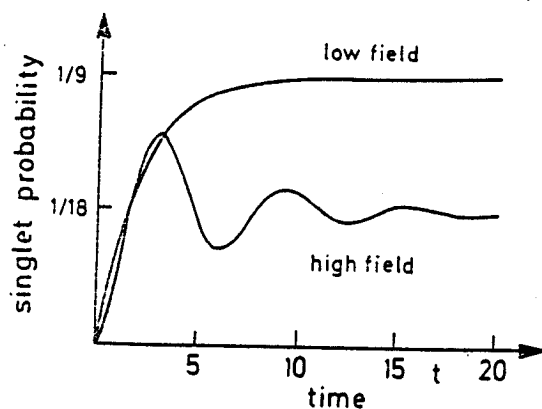


FIG. 7. Singlet probability of a triplet-triplet encounter pair as in Fig. 6(b) with $E \neq 0$ at low and high field for an ensemble in which both triplets undergo orientational relaxation with $\tau_r = 0.5$, the correlation functions ${}^3c_1(t)$, ${}^3c_2(t)$, and ${}^3C(t)$ were evaluated according to Eqs. (3.12), (3.13), and (3.15), respectively.

induce an equipartition of all degenerate spin states. Initially all eight triplet and quintet states are populated. At low fields and if the zero field splitting is neglected these states are all degenerate with the overall singlet state of ${}^3T_1 + {}^3T_2$. The zero field splitting leads to a population of the singlet state. Equipartition implies then the fraction $\frac{1}{3}$ of singlet character in agreement with the exact result.

In order to explain the asymptotic value $\frac{1}{18}$ in the high field situation one can again invoke asymptotic phase randomization as an explanation, albeit in a modified manner. At high fields without zero field splitting only two of the eight triplet and quintet states, T_0 and Q_0 , are degenerate with the singlet state S_0 . In the basis of triplet-triplet product states

$$|1\rangle = |1, -1\rangle|1, +1\rangle, |2\rangle = |1,0\rangle|1,0\rangle$$

and

$$|3\rangle = |1, +1\rangle|1, -1\rangle$$

these three states are

$$|Q_0\rangle = (|1\rangle + 2|2\rangle + |3\rangle)/\sqrt{6},$$

$$|T_0\rangle = (-|1\rangle + |3\rangle)/\sqrt{2}, |S_0\rangle = (|1\rangle - |2\rangle + |3\rangle)/\sqrt{3}.$$

However, before one applies the idea of phase randomization it is important to observe that according to Eqs. (2.29a), and (2.29b) the $|1,1\rangle$ and $|1, -1\rangle$ states of an individual triplet for any particular realization of orientation specified by θ, ϕ experience identical phase changes. [See also the comment below Eq. (2.32).] This implies that the phase difference of $|1\rangle$ and $|3\rangle$ produced by the zero field splitting interaction upon the initial overall triplet and quintet states must vanish. Except for an overall phase factor the zero field splitting produces then the transition

$$\begin{aligned} |T_0\rangle &\rightarrow |T_0\rangle, |Q_0\rangle \rightarrow |Q_0(\phi)\rangle \\ &= (|1\rangle + 2 \exp(i\phi)|2\rangle + |3\rangle)/\sqrt{6}, \end{aligned}$$

i.e., only the quintet state assumes singlet character

$$|\langle S_0 | Q_0(\phi) \rangle|^2 = \frac{1}{3}(1 - \cos \phi).$$

The assumption of a random phase yields then

$$|\langle S_0 | Q_0(\phi) \rangle|^2 = \frac{1}{3}.$$

Since only $\frac{1}{3}$ of the initial population is in the state $|Q_0\rangle$ one arrives at the correct asymptotic singlet probability $\frac{1}{3} \cdot \frac{1}{3} = \frac{1}{18}$.

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¹For a most recent review of magnetic field effects connected with doublet pair processes in chemistry and biology see K. Schulten, *Advances in Solid State Physics*, edited by J. Treusch (Vieweg, Braunschweig, 1982), Vol. XXII, p. 62; R. Z. Sagdeev, K. M. Salikhov, and Yu. M. Molin, *Russ. Chem. Rev.* **46**, 297 (1977).

²G. J. Hoytink, *Discuss. Faraday Soc.* **45**, 14 (1968); L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.* **91**, 6497 (1969).

³L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.* **91**, 6495 (1969); P. Avakian, R. P. Groff, E. E. Kellogg, R. E. Merrifield, and A. Suna in *Organic Scintillators and Liquid Scintillation Counting* (Academic, New York, 1971), p. 499; H. Tachikawa and A. J. Bard, *Chem. Phys. Lett.* **26**, 10 (1974); J. Spichtig, H. Bulska, and H. Labhart, *Chem. Phys.* **15**, 279 (1976) and references therein.

⁴Z. Schulten and K. Schulten, *J. Chem. Phys.* **66**, 4616 (1977).

⁵R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.* **4**, 195, 214 (1969); G. L. Closs, *J. Am. Chem. Soc.* **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *J. Am. Chem. Soc.* **92**, 2183, 2186 (1970); *Chemically Induced Magnetic Polarization* edited by L. T. Muus, P. W. Atkins, K. A. McLaughlan, and J. B. Pedersen (Reidel, Dordrecht, 1977).

⁶K. Schulten and P. G. Wolynes, *J. Chem. Phys.* **68**, 3292 (1978); E.-W. Knapp and K. Schulten, *J. Chem. Phys.* **71**, 1878 (1979).

⁷K. Schulten, H. Staerk, A. Weller, H.-J. Werner, and B. Nickel, *Z. Phys. Chem. NF* **101**, 371 (1976); M. E. Michel-Beyerle *et al.*, *Chem. Phys.* **17**, 139 (1976); early triplets, however, attributed to relaxation in a triplet exciplex were reported in M. Ottolenghi, *Acc. Chem. Res.* **6**, 153 (1973); N. Orbach and M. Ottolenghi, *Chem. Phys. Lett.* **35**, 175 (1975); N. Orbach and M. Ottolenghi in *The Exciplex*, edited by M. Gordon and W. R. Ware (Academic, New York, 1975), p. 75.

⁸H.-J. Werner, Z. Schulten, and K. Schulten, *J. Chem. Phys.* **67**, 646 (1977); H.-J. Werner, H. Staerk, and A. Weller, *J. Chem. Phys.* **68**, 2419 (1978).

⁹K. Schulten and I. R. Epstein, *J. Chem. Phys.* **71**, 309 (1979).

¹⁰K. Lendi, P. Gerber, and H. Labhart, *Chem. Phys.* **18**, 449 (1976).

¹¹J. Barber, *Primary Processes in Photosynthesis* (North-Holland, Amsterdam, 1977).

¹²A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1957).

¹³N. Abramowitz and I. A. Stegun, *Appl. Math. Ser.* **55**, (1965).

¹⁴P. Debye, *Trans. Electrochem. Soc.* **82**, 205 (1942).

¹⁵R. G. Gordon, *J. Chem. Phys.* **44**, 1830 (1966).

¹⁶K. Schulten, Z. Schulten, and A. Szabo, *J. Chem. Phys.* **74**, 4426 (1981).

¹⁷F. Nolting, H. Staerk, and A. Weller, *Chem. Phys. Lett.* **88**, 523 (1982); H. Staerk, R. Treichel, and A. Weller, *ibid.* **96**, 28 (1983).

¹⁸K.-P. Charlé and F. Willig, in *Magnetic Effects in Reaction Kinetics* (to be published).