Semiclassical description of electron spin motion in radicals including the effect of electron hopping

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The coherent electron spin motion in radicals induced by the hyperfine coupling to nuclear spins is described semiclassically. The nuclear spins are treated as constant classical vectors around which the electron spin precesses. The ensemble average over all nuclear spin configurations is taken yielding the electron spin correlation tensor $\langle S(0)S(t)\rangle$. Borrowing from the theory of rotational diffusion the effect of electron hopping between molecules on the spin correlation tensor is described. The treatment is applied to the time evolution of the electron spin state of a radical pair initially prepared in a singlet state.

I. INTRODUCTION

The unpaired electron spins in free radicals carry out a coherent motion which is induced by the hyperfine interaction between electron and nuclear spins. The motion entails the precession of the electron spin around the combination of nuclear spins with a frequency of 1/10 ns^{-1} to 1/100 ns^{-1} depending on the strength of the hyperfine coupling. When radical *pairs* are generated in a well-defined electron spin state, e.g., a singlet spin state, this motion can be observed through the radical recombination products the spin multiplicity of which is determined by the relative orientation of the electron spins at the instance of recombination. External magnetic fields alter the electron spin motion and, thereby, also the yields of (singlet vs triplet) recombination products.[1] An analysis of the observed magnetic field effect can yield valuable information about the microscopic diffusion of the radical pair over the time period of a few nanoseconds, about the solvent mediated force field between the radicals and the reaction propensities to singlet and triplet products.[2,3] For such analysis one needs an accurate knowledge of the relative orientation of the electron spin, as a function of time. In principle this can be predicted on the basis of the hyperfine coupling constants known from ESR spectra[2,4] but for radicals with large numbers of nuclear spins the quantum mechanical analysis is cumbersome if not impossible.

Calculations carried out for large nuclear spin systems have shown, however, a remarkably simple functional behavior of the electron spin probability of radical pair ensembles. This comes about through the average taken over all nuclear spin configurations of the pairs. The results suggest that one may employ with advantage a method of directly evaluating the average spin probability without taking recourse to the details of the electron spin motion in the various nuclear spin configurations. In fact, a very simple expression of the triplet probability of radical pairs at high fields had been derived previously.[4] In this paper we provide a theory for the average electron spin motion for arbitrary fields and provide a simple analytical description for the case of zero magnetic field.

The theory provided in this paper is based on the observation that in a radical with a large nuclear spin system hyperfine coupled to the unpaired electron spin on the average, the total nuclear spin is much larger than the electron spin $\frac{1}{2}$. Hence, the hyperfine-induced precession of electron and nuclear spins around each other leaves the nuclear spin approximately unaltered. This leads us to treat the nuclear spins as classical vectors and to describe the electron spin motion as a precession around the *constant* vector resulting from a linear combination of nuclear spins and external field B as illustrated in Fig. 1 for the radical pair pyrene–N, N-dimethylaniline ($^2Py^- + ^2DMA^+$). The electrons in the separate radicals precess with different frequencies around axes oriented differently in space and, thereby, change their relative orientation. The nuclear spin contribution to the electron spin precession depends on the nuclear spin configuration represented in Fig. 1 by the polymer-type vector sums of the nuclear magnetic moments. The averaging over the nuclear spin configurations indeed will follow the statistical treatment of polymers.[5]

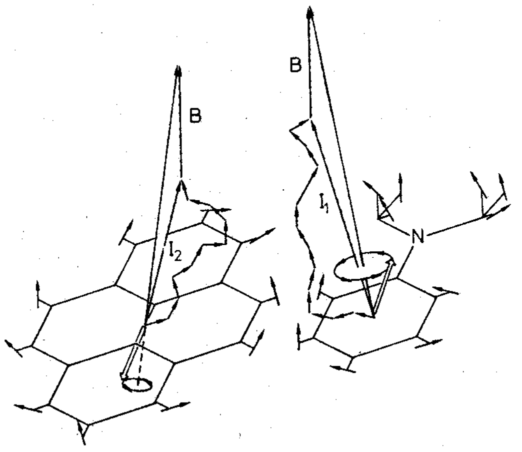

FIG. 1. Schematic illustration of the electron spin precession in the pyrene–dimethylaniline ($^2Py^- + ^2DMA^+$) radical pair.

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The theory described allows us to include in a simple manner the effect of the hopping of the unpaired electrons between different molecules. After a jump the unpaired electron finds a new, random nuclear spin configuration. The hopping may then be described as a random change in the direction and rate of precession of the electron spin. As the motion of the precessing electron spin is reminiscent of the motion of a freely rotating molecule, it is not surprising that the spin motion of the hopping electron turns out to be mathematically equivalent to a molecule undergoing rotational diffusion. Our treatment can therefore use the theory of the latter process as developed by Gordon.[6]

II. SEMICLASSICAL DESCRIPTION OF THE HYPERFINE-INDUCED SPIN MOTION

The Hamiltonian which governs the hyperfine coupling induced spin motion in radical 1 and 2 is

$$H = H_1 + H_2, \tag{1}$$

where ($i = 1, 2$)

$$H_i = \omega_0 S_{1z} + \sum_k a_{ik} \mathbf{I}_{ik} \cdot \mathbf{S}_i\,, \tag{2}$$

and

$$\omega_0 = g\mu B/\hbar\,, \tag{3}$$

is the Larmor frequency of an electron in the magnetic field B aligned along the z axis. The Hamiltonian assumes for simplicity identical g values for the two unpaired electrons in the radical pair, includes only the isotropic part of the hyperfine coupling tensors and neglects the weak nuclear spin Zeeman interaction.

The starting point for our semiclassical description of the electron spin motion is to treat in (2)

$$\mathbf{I}_i = \sum_k a_{ik} \mathbf{I}_{ik} \tag{4}$$

as a *constant* classical vector not affected by the electron–nuclear spin interaction, i.e., the electron spin $\mathbf{S}_i$ is precessing around the vector

$$\omega_i = \mu g \mathbf{B}/\hbar + \mathbf{I}_i, \tag{5}$$

with frequency ω_i. In reality both $\mathbf{S}_i$ and ω_i change with time but for large nuclear spin systems one can assume the variation of $\mathbf{I}_i$ and, therefore, of ω_i to be negligible. This assumption limits, however, the applicability of our description to radicals with large nuclear spin systems, i.e., it complements in this respect the exact quantum mechanical description possible only for small nuclear spin systems.

As pointed out above we seek to describe the electron spin motion for an ensemble of radical pairs which includes all possible nuclear spin configurations. The statistical distribution of $\mathbf{I}_i$ for all nuclear spin orientations on radical i corresponds to the distribution of the end-to-end distance of a freely jointed polymer (see Fig. 1) with "bond lengths" $a_{ik}[I_{ik}(I_{ik}+1)]^{1/2}$. One has for the end-to-end distribution in the volume element $\mathbf{I}_i + d\mathbf{I}_i$ (see Ref. 5)

$$f(\mathbf{I}_i) = (\tau_i^2/4\pi)^{3/2} \exp(-\tfrac{1}{4} I_i^2 \tau_i^2)\,, \tag{6}$$

where

$$\tau_i^{-1} = \frac{1}{6} \sum_k a_{ik}^2 I_{ik}(I_{ik}+1) \tag{7}$$

and I_{ik} denotes the nuclear spin quantum number, e.g., $\frac{1}{2}$ (1) for proton (nitrogen). The Gaussian form of this distribution is only accurate if the mean square effective magnetic moment of the nuclei τ_i^{-2} is very much larger than the contribution due to any single spin $a_{ik}I_{ik}(I_{ik}+1)$. Therefore, Eq. (6) cannot be expected to yield a good description for the distribution of $\mathbf{I}_i$ in case that one or only a few nuclear spins give a dominant contribution to the hyperfine coupling.

The triplet probability of an ensemble of radical pairs initially ($t = 0$) in a singlet state is

$$p_T(t) = \langle \operatorname{tr}[Q_S(0)\, Q_T(t)]\rangle, \tag{8}$$

where

$$\begin{aligned} Q_S(t) &= \tfrac{1}{4} - \mathbf{S}_1(t) \cdot \mathbf{S}_2(t), \\ Q_T(t) &= \tfrac{3}{4} + \mathbf{S}_1(t) \cdot \mathbf{S}_2(t), \end{aligned} \tag{9}$$

are the projection operators (at time t) on the singlet and triplet electron spin state, respectively. tr denotes the sum over all expectation values of the electron spin states and $\langle\ \rangle$ stands for the average over all nuclear spin configurations

$$\langle A(\mathbf{I}_1, \mathbf{I}_2)\rangle = \int d\mathbf{I}_1 \int d\mathbf{I}_2 f(\mathbf{I}_1) f(\mathbf{I}_2) A(\mathbf{I}_1, \mathbf{I}_2). \tag{10}$$

This representation of the triplet probability as an equilibrium time correlation function Eq. (8) is completely general and can be used as a convenient starting point no matter what the mechanism of spin motion. With the spin Hamiltonian chosen here, the time correlation function expression for p_T can be written in a form which allows us to take the averages corresponding to each of the radicals separately

$$p_T(t) = \tfrac{3}{4} - {}_1\mathbf{T} : {}_2\mathbf{T}, \tag{11}$$

where ${}_i\mathbf{T}$ denotes the spin correlation tensor

$${}_i\mathbf{T} = \langle \operatorname{tr} \mathbf{S}_i(0) \mathbf{S}_i(t)\rangle\,, \tag{12}$$

the trace being taken only over the electron spin state of radical i. The tensor product : in the S_{i+}, S_{i-}, S_{iz} representation is defined as follows

$$\begin{aligned} {}_1\mathbf{T} : {}_2\mathbf{T} = \tfrac{1}{4}({}_1T_{++}\,{}_2T_{--} &+ {}_1T_{+-}\,{}_2T_{-+} + {}_1T_{-+}\,{}_2T_{+-} \\ &+ {}_1T_{--}\,{}_2T_{++}) + \tfrac{1}{2}({}_1T_{+z}\,{}_2T_{-z} + {}_1T_{-z}\,{}_2T_{+z} \\ &+ {}_1T_{z+}\,{}_2T_{z-} + {}_1T_{z-}\,{}_2T_{z+}) + {}_1T_{zz}\,{}_2T_{zz}. \end{aligned} \tag{13}$$

{In deriving (11) we have used $\operatorname{tr}[\mathbf{S}_1(t) \cdot \mathbf{S}_2(t)] = 0$.}

III. EVALUATION OF $\mathbf{T} = \langle \operatorname{tr}[\mathbf{S}(0)\,\mathbf{S}(t)]\rangle$

We wish to determine now the time behavior of the spin correlation tensor (12) (we omit the index i in this section). The spin operator $\mathbf{S}(t)$ obeys the equation of motion

$$\frac{d}{dt}\mathbf{S}(t) = \omega \times \mathbf{S}(t), \tag{14}$$

where ω is defined by Eq. (5). The solution of this equation which describes the precession of $\mathbf{S}$ around $\boldsymbol{\omega}$ is

$$\mathbf{S}(t)=\mathbf{U}(t)\mathbf{S}(0)\mathbf{U}(-t), \tag{15}$$

where $\mathbf{U}(t)$ is a rotation matrix in the spin $\frac{1}{2}$ representation

$$\mathbf{U}(t)=\begin{pmatrix} v & iwx \\ iw\bar{x} & \bar{v} \end{pmatrix}, \tag{16}$$

where

$$v=\cos^2\theta/2\exp(i\omega t/2)+\sin^2\theta/2\exp(-i\omega t/2), \tag{17}$$

$$w=-\sin\theta\sin(\omega t/2), \tag{18}$$

$$x=\exp(i\phi), \tag{19}$$

and the angles θ and ϕ define the orientation of $\boldsymbol{\omega}$. Eq. (15) then yields

$$S_+(t)=\begin{pmatrix} -iwv\bar{x} & v^2 \\ w\bar{x}^2 & iwv\bar{x} \end{pmatrix}, \tag{20}$$

$$S_-(t)=\begin{pmatrix} iw\bar{v}x & w^2x^2 \\ \bar{v}^2 & -iw\bar{v}x \end{pmatrix}, \tag{21}$$

$$S_z(t)=\frac{1}{2}\begin{pmatrix} v\bar{v}-w^2 & -2iwvx \\ 2iw\bar{v}\bar{x} & w^2-v\bar{v} \end{pmatrix}. \tag{22}$$

In these expressions the average over the azimuthal angle ϕ can be carried out immediately. Since $\langle x\rangle=\langle\bar{x}\rangle=\langle x^2\rangle=\langle\bar{x}^2\rangle=0$ one obtains

$$\mathbf{T}=\mathrm{tr}\,[\mathbf{S}(0)\mathbf{M}^{(0)}\mathbf{S}(0)], \tag{23}$$

where $\mathbf{M}^{(0)}(t)$ assumes a diagonal form

$$\mathbf{M}^{(0)}(t)=\begin{pmatrix} \langle v^2\rangle & 0 & 0 \\ 0 & \langle\bar{v}^2\rangle & 0 \\ 0 & 0 & \langle v\bar{v}-w^2\rangle \end{pmatrix}. \tag{24}$$

In the case of zero field and high field the averages in (24) can be evaluated readily. At zero field one finds

$$\mathbf{M}^{(0)}(t)=\tfrac{1}{3}[1+2C(t/\tau)]\,\mathbf{1}, \tag{25}$$

where

$$C(x)=(1-2x^2)\exp(-x^2), \tag{26}$$

and τ is defined as in Eq. (7). At high fields one has $\theta=0$ and, hence, $v^2=\exp(i\omega t)$ and $v\bar{v}-w^2=1$. The average of $e^{i\omega t}$ is in cylindrical coordinates

$$\langle e^{i\omega t}\rangle=2\pi\left(\frac{\tau^2}{4\pi}\right)^{3/2}\int_0^\infty dI_\rho I_\rho \times\int_{-\infty}^\infty dI_z\exp[-\tfrac{1}{4}(I_\rho^2+I_z^2)\tau^2]\exp(i\omega t). \tag{27}$$

By virtue of $\omega=[(\omega_0+I_z)^2+I_\rho^2]^{1/2}\approx\omega_0+I_z$, which holds in the limit of large ω_0 one obtains

$$\langle e^{i\omega t}\rangle=\exp(i\omega_0 t)\frac{\tau}{\sqrt{\pi}}\int_{-\infty}^\infty dI_z\exp(-\tfrac{1}{4}I_z^2\tau^2+iI_zt), \tag{28}$$

and hence,

$$\mathbf{M}^{(0)}(t)=\begin{pmatrix} e^{i\omega_0 t}e^{(0)}(t/\tau) & 0 & 0 \\ 0 & e^{-i\omega_0 t}e^{(0)}(t/\tau) & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{29}$$

where

$$e^{(0)}(x)=\exp(-x^2). \tag{30}$$

IV. HYPERFINE COUPLING-INDUCED TRIPLET PROBABILITY WITHOUT ELECTRON HOPPING

The evaluation of the tensor $\mathbf{T}$ for zero field and high field leads by virtue of Eqs. (11) and (13) to the following analytical expressions for the triplet probabilities:

Zero field,

$$p_T(t)=\tfrac{3}{4}[1-g^{(0)}(t/\tau_1)g^{(0)}(t/\tau_2)], \tag{31}$$

$$g^{(0)}(x)=\tfrac{1}{3}[1+2C(x)]. \tag{32}$$

High field,

$$p_T(t)=\tfrac{1}{2}[1-e^{(0)}(t/\tau_1)e^{(0)}(t/\tau_2)]. \tag{33}$$

In Fig. 2 we compare for the $^2\mathrm{Py}^-+^2\mathrm{DMA}^+$ radical pair these expressions with the triplet probabilities resulting from the exact quantum mechanical treatment in Ref. 4. One finds excellent agreement between the quantum mechanical results (which in the zero field case involve great numerical effort) and the semiclassical predictions (31) and (33). As $\lim_{x\to\infty}g(x)=\frac{1}{3}$ the triplet probability at zero field assumes asymptotically the value $\frac{2}{3}$. This is in agreement with the quantum mechanical calculation taken at 40 ns. As this calculation describes a coherent motion, however, it exhibits further oscillations at longer times. One can expect (31) and (33) to be valid for times $t<\min(\pi/a_{ik})$.

The expression (31) yields an immediate interpretation of the oscillations of $p_T(t)$ at zero field in Fig. 3.

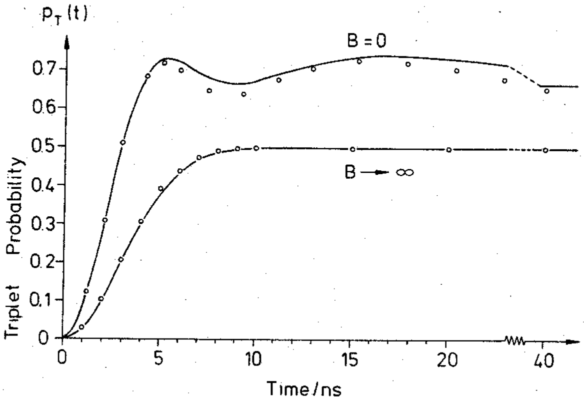

FIG. 2. Comparison of the triplet probability of the unpaired electron spins in $^2\mathrm{Py}^-+^2\mathrm{DMA}^+$ predicted by the semiclassical approximation, i.e., Eqs. (31) and (33), [—] and evaluated from an exact quantum mechanical analysis (Ref. 4) [o]. Hyperfine coupling constants assumed are Py: $4\times(a_\mathrm{H}=2.3\ \mathrm{G})$, $4\times(a_\mathrm{H}=5.2\ \mathrm{G})$; DMA: $6\times(a_{\mathrm{CH}_3}=12.0\ \mathrm{G})$, $1\times(a_\mathrm{N}=12.0\ \mathrm{G})$, $3\times(a_\mathrm{H}=6.25\ \mathrm{G})$.

These features are due to the functions $g(t/\tau_1)$ and $g(t/\tau_2)$ which describe damped oscillations originating from the precession of the electron spins $\mathbf{S}_1$ and $\mathbf{S}_2$ with various precession frequencies and around various axes. These oscillations are totally analogous to the dips observed in the orientational correlation functions of free rotors in the gas phase.[6] The first oscillation in Fig. 3 is due to the electron spin on the ^{2}DMA$^+$ radical with an τ_1 value of 4.35 ns. The second oscillation is due to the ^{2}Py$^-$ radical with weaker hyperfine coupling and, therefore, a larger τ_2 value of 14.13 ns.

V. HOPPING OF PRECESSING ELECTRON

We want to evaluate now the spin correlation tensor $\mathbf{T} = \langle \mathbf{S}(0)\mathbf{S}(t)\rangle$ for the case that the electron is not residing permanently on one molecule but is jumping between different molecules. The correlation tensor without jumping has been determined for the case of zero and high field in Sec. III. When jumping occurs one must further average over all possible sequences of jumping events. To describe this, we employ the theory of rotational diffusion pioneered by Gordon[6] and outlined in Ref. 7. Let us denote by $\mathbf{T}_n(t)$ the contribution to $\mathbf{T}(t)$ due to electrons which have undergone $n-1$ jumping events up to time t so that

$$\mathbf{T}(t) = \sum_{n=1}^{\infty} \mathbf{T}_n(t) \equiv \left\langle \operatorname{tr}\left[\mathbf{S}(0) \sum_{n=1}^{\infty} \mathbf{M}^{(n)}(t)\,\mathbf{S}(0)\right]\right\rangle. \tag{34}$$

The jumping events are assumed to be independent and to occur by first order kinetics. The mean residence time is τ_0. The probability of not observing a jump by time t is then $\exp(-t/\tau_0)$ and, therefore, the time evolution of $\mathbf{S}(t)$ without jump is described by

$$\mathbf{M}^{(1)}(t) = \exp(-t/\tau_0)\,\mathbf{M}^{(0)}(t). \tag{35}$$

Because the jumping events are independent, the following recurrence relation holds

$$\mathbf{M}^{(n)}(t) = \tau_0^{-1}\int_0^t dt'\,\mathbf{M}^{(1)}(t-t')\,\mathbf{M}^{(n-1)}(t') \tag{36}$$

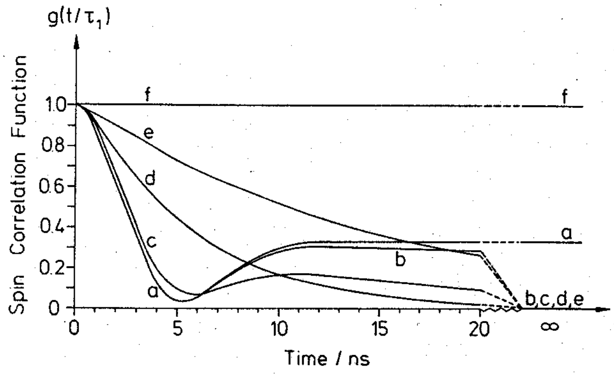

FIG. 3. Time dependence of the spin correlation function $g(t/\tau_1)$ of the unpaired electron in ^{2}DMA$^+$ ($\tau_1 = 4.35$ ns) for various residence times τ_0: (a) $\tau_0 \to \infty$; (b) $\tau_0 = 100$ ns; (c) $\tau_0 = 10$ ns; (d) $\tau_0 = 1$ ns; (e) $\tau_0 = \frac{1}{3}$ ns; (f) $\tau_0 = 0$. The hyperfine coupling constants assumed are given below Fig. 2.

For $B = 0$ this becomes

$$\mathbf{M}^{(n)}(t) = g^{(n)}(t/\tau)\,\mathbf{1}, \tag{37}$$

where

$$g^{(1)}(t/\tau) = \tfrac{1}{3}[1 + 2C(t/\tau)]\exp(-\lambda t/\tau), \tag{38}$$

and

$$g^{(n)}(t/\tau) = \lambda \int_0^{t/\tau} dx\, g^{(1)}\left(\frac{t}{\tau} - x\right) g^{(n-1)}(x), \tag{39}$$

$$\lambda = \tau/\tau_0. \tag{40}$$

For $B \to \infty$ the time evolution operators have the form

$$\mathbf{M}^{(n)}(t) = \begin{pmatrix} e^{i\omega_0 t}\, e^{(n)}(t/\tau) & 0 & 0 \\ 0 & e^{-i\omega_0 t}\, e^{(n)}(t/\tau) & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{41}$$

where

$$e^{(1)}(t/\tau) = e^{(0)}(t/\tau)\exp(-\lambda t/\tau), \tag{42}$$

$$e^{(n)}(t/\tau) = \lambda \int_0^{t/\tau} dx\, e^{(1)}\left(\frac{t}{\tau} - x\right) e^{(n-1)}(x). \tag{43}$$

In the case that only one of the unpaired electrons of a radical pair engages in the hopping between the molecules constituting radical 1, the triplet probabilities (31) and (33) assume the form

Zero field,

$$p_T(t) = \tfrac{3}{4}[1 - g(t/\tau_1)\,g^{(0)}(t/\tau_2)], \tag{44}$$

$$g(t/\tau_1) = \sum_{n=1}^{\infty} g^{(n)}(t/\tau_1). \tag{45}$$

High field,

$$p_T(t) = \tfrac{1}{2}[1 - e(t/\tau_1)\,e^{(0)}(t/\tau_2)], \tag{46}$$

$$e(t/\tau_1) = \sum_{n=1}^{\infty} e^{(n)}(t/\tau_1). \tag{47}$$

Unfortunately, the functions $g(x)$ and $e(x)$ cannot be expressed in analytical form. They can be evaluated numerically, however, according to a scheme suggested by Gordon.[6] This scheme involves discretization of x, i.e., $x \to x_0 = 0, x_1, x_2, \ldots$, replacing thereby the function $g^{(n)}(x)$, for example, by the vector $\mathbf{G}^{(n)}$ with components

$$G_k^{(n)} = g^{(n)}(x_k), \tag{48}$$

and the convolution (39) by the matrix operation

$$\mathbf{G}^{(n)} = \mathbf{A}\mathbf{G}^{(n-1)}, \tag{49}$$

where $\mathbf{A}$ is a tridiagonal matrix the elements of which are determined by the choice of numerical approximation to the integrals in Eq. (39). One obtains then

$$\mathbf{G} = \sum_{n=1}^{\infty} \mathbf{G}^{(n)} = (\mathbf{1} - \mathbf{A})^{-1}\,\mathbf{G}^{(1)}, \tag{50}$$

where the evaluation of the inverse of $\mathbf{1} - \mathbf{A}$ is a simple matter as the matrix is tridiagonal. The functional behavior of the function $g(t/\tau_1)$ (τ_1 corresponding to the ^{2}DMA$^+$ radical) for various τ_0 values is presented in Fig. 3. For long residence times $\tau_0 \gg \tau_1$ one finds $g(t/\tau_1)$ to approach $g^{(0)}(t/\tau_1)$ which is to be expected since $g^{(0)}(t/\tau_1)$ describes the spin correlation for infinite residence time. A finite τ_0 induces, however, a decay of $g(t/\tau_1)$ to zero at long times. For very small τ_0 $g(t/\tau_1)$ approaches the value 1, i.e., the electron is hopping so frequently that the spin precession comes to a halt due to an effectively zero hyperfine interaction.

The functional behavior of $g(t/\tau_1)$ can be illustrated also by means of its Laplace transform

$$\hat{g}(s) = \int_0^\infty dx\, e^{-sx} g(x), \tag{51}$$

which can be evaluated readily according to Eqs. (38) and (39) from

$$\hat{g}^{(1)}(s) = \hat{g}^{(0)}(s + \tau_1/\tau_0), \tag{52}$$

$$\hat{g}^{(n)}(s) = \frac{\tau_1}{\tau_0} \hat{g}^{(0)}\left(s + \frac{\tau_1}{\tau_0}\right) \hat{g}^{(n-1)}(s). \tag{53}$$

This yields immediately

$$\hat{g}(s) = \frac{g^{(0)}(s + \tau_1/\tau_0)}{1 - (\tau_1/\tau_0)\hat{g}^{(0)}(s + \tau_1/\tau_0)} . \tag{54}$$

For $\tau_1/\tau_0 \to 0$, i.e., infinite residence time τ_0, one has $\hat{g}(s) = g^{(0)}(s)$ and, hence, $g(t/\tau_1) = g^{(0)}(t/\tau_1)$. We can also use this representation to discuss the case of very rapid hopping, i.e., $\tau_1/\tau_0 \to \infty$. In this limit we need retain only the short time behavior of $g^{(0)}(t)$ since the Laplace transform is to be evaluated at large argument, that is

$$\begin{aligned} \hat{g}^{(0)}\left(s + \frac{\tau_1}{\tau_0}\right) &= \int_0^\infty \exp\left[-\left(s + \frac{\tau_1}{\tau_0}\right)x\right] g^{(0)}(x)\, dx \\ &\simeq \int_0^\infty \exp\left[-\left(s + \frac{\tau_1}{\tau_0}\right)x\right] (1 - 2x^2 + \cdots)\, dx \\ &= \frac{1}{s + \frac{\tau_1}{\tau_0}} - \frac{4}{\left(s + \frac{\tau_1}{\tau_0}\right)^3} + \cdots . \end{aligned} \tag{55}$$

The fact that only the short time behavior of $g^{(0)}(t)$ is involved is related to the fact that the electron spin can only precess for a short time before a jump randomizing the nuclear spin configuration occurs. Substituting this approximation for $g^{(0)}(s)$ into the expression for $g(s)$, we obtain

$$\begin{aligned} g(s) &= \frac{1}{\dfrac{1}{\left(s + \frac{\tau_1}{\tau_0}\right)^{-1} - \dfrac{4}{\left(s + \frac{\tau_1}{\tau_0}\right)^3}} - \dfrac{\tau_1}{\tau_0}} \\ &= \frac{1}{\left(s + \frac{\tau_1}{\tau_0}\right) \dfrac{1}{1 - \dfrac{4}{\left(s + \frac{\tau_1}{\tau_0}\right)^2}} - \dfrac{\tau_1}{\tau_0}} . \end{aligned} \tag{56}$$

If τ_1/τ_0 is very large $4/(s + \tau_1/\tau_0)^2$ is quite small, in which case $\hat{g}(s)$ has the simple form

$$\hat{g}(s) = \frac{1}{\left(s + 4\frac{\tau_0}{\tau_1}\right)} . \tag{57}$$

This implies that $g(t)$ decays exponentially

$$g\left(\frac{t}{\tau_1}\right) = \exp\left(-\frac{4\tau_0}{\tau_1} \frac{t}{\tau_1}\right). \tag{58}$$

This exponential decay of g is just what is expected for the small step diffusion of the electron spin vector due to the rapidly varying hyperfine interaction when the electron jumps often. As such, it is also the form that would be predicted by the simple relaxation theories which assume fast modulation.

Even when the decay of g to zero is not exponential, this decay can be usefully characterized by the correlation time τ_c, defined by

$$\tau_c = \int_0^\infty g\left(\frac{t}{\tau_1}\right) dt . \tag{59}$$

For large residence times $\tau_c \sim \tau_0/2$, i.e., τ_c tends to infinity as is to be expected from the fact that $g^{(0)}(t/\tau_1)$ assumes asymptotically a nonzero value. If the residence time is short the decay of g is also slow, as shown in Eq. (58) and τ_c also tends to infinity as $\tau_0 \to 0$. That is, for an infinitely rapid hopping process, $g(t)$ becomes essentially 1, for any finite time.

In Fig. 4 we present the triplet probability for the $^2\mathrm{Py}^- + {}^2\mathrm{DMA}^+$ radical pair at zero and high field for the case that the $^2\mathrm{DMA}^+$ electron is hopping. Figure 4 demonstrates that electron hopping slows down the singlet–triplet transition at short times. At long times the hopping process changes the asymptotic behavior of $p_T(t)$ which assumes the asymptotic

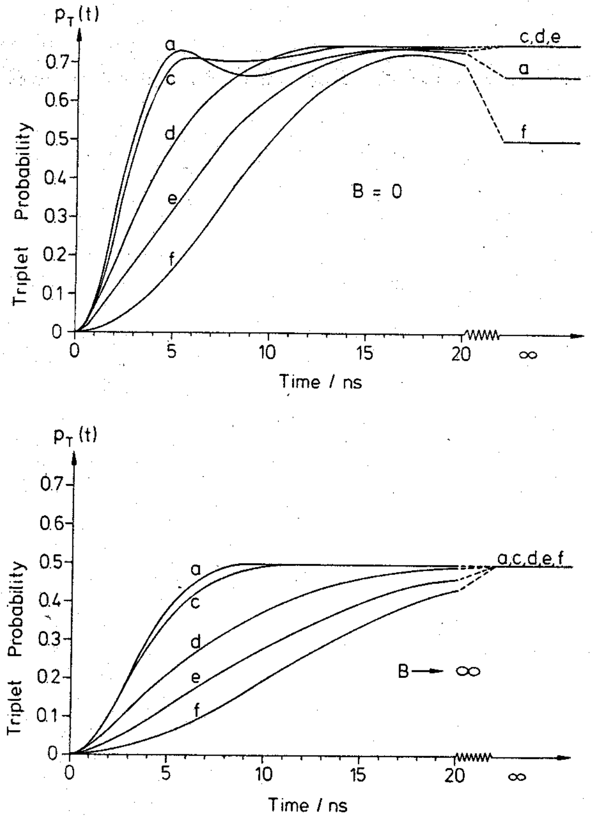

FIG. 4. Triplet probability of the $^2\mathrm{Py}^-$ and $^2\mathrm{DMA}^+$ radical pair in case of electron hopping between DMA for various residence times τ_0 at zero field and high field. For designation of the curves, i.e., residence times of the $^2\mathrm{DMA}^+$ unpaired electrons, see Fig. 3. The residence time of the $^2\mathrm{Py}^-$ unpaired electron is assumed to be infinite. Hyperfine coupling constants are given below Fig. 2.

value $\frac{2}{3}$. If the hopping of the ^{2}DMA$^+$ electron is infinitely rapid, the orientation of that electron spin will remain fixed and the asymptotic value of the triplet probability becomes $\frac{1}{2}$. In general, for a finite but nonzero residence time, the asymptotic value is $\frac{3}{4}$, a result which can be derived from Eq. (44). In the case of high magnetic fields, the asymptotic value $\frac{1}{2}$ is not altered by the hopping process which shows clearly that the effect of electron hopping at longer times depends on the applied magnetic field. An effect of an applied field on electron spin relaxation of radical pairs in systems where electron hopping is expected has been observed by Klein and Voltz.[8]

The residence time τ_0 is inversely proportional to the concentration of the molecular species between which the electron hopping takes place. If the electron transfer is a diffusion controlled process one has

$$\tau_0^{-1} = 4\pi D r_1 c_1, \tag{60}$$

where D is the diffusion constant, r_1 the distance at which electron transfer takes place, and c_1 the concentration. Assuming $D = 10^{-5}$ cm^2 s^{-1} and $r_1 = 7$ Å curve d in Fig. 4 corresponds to a DMA concentration of 0.2 mol l^{-1}. This example demonstrates that in many instances, especially when electron hopping can take place between the solvent molecules, the hyperfine-induced spin motion should be affected by electron transfer processes.

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