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The Theory of Chemically Induced Dynamic Spin Polarization

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I. Introduction

In this paper we wish to present the theory for the very interesting phenomenon of chemically induced dynamic spin polarization. We shall consider both the NMR case of chemically induced dynamic nuclear (spin) polarization (CIDNP) and the ESR case of chemically induced dynamic electron (spin) polarization (CIDEP). This subject, which involves a combination of magnetic resonance and spin-selective reaction dynamics in liquid solution, now has a large literature associated with it including reviews and books.[1–4] We will not try to summarize this literature here; the reader is referred instead to the other sources especially for the extensive experimental results. We offer a single coherent and unified treatment of the main theory. That is, we approach the problem from a very general formulation, known as the stochastic Liouville equation (SLE), in which both the spin dynamics and the diffusive and reactive dynamics can be treated simultaneously and in great detail.[4–9] The many earlier simplified theoretical analyses of the radical-pair mechanism (RPM) are in fact found to be based upon simplified submodels, which are all naturally included in precisely their correct relative importance in the general treatment.

In our solution of the appropriate SLE, we have employed numerical techniques extensively.[5–9] This approach allows virtually unlimited choice in the selection of the features of the models; thus analyses may be made without necessarily requiring specialized limiting conditions, and the generality of the results may be examined in the light of the different possible descriptions. It turns out, furthermore, that an analysis of these results is often able to yield exact (as well as approximate) basic relationships for the description of the CIDNP and CIDEP phenomena, which are of considerable utility. The dependence of these relationships (and the corrections to them) on the many details of the models can then be studied. From this analysis, a fairly clear picture of the basic nature and physical details of chemically induced dynamic spin polarization by the RPM emerges, and this is also discussed. It is seen that the basic reencounter mechanism, wherein radical

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[2] A. L. Buchachenko, "Khimicheskaya Polyarizatziya Elektronov Ee Yader." Moscow, 1974.
[3] R. G. Lawler, *Prog. Nucl. Magn. Resonance Spectrosc.* 9, Part 3, 145 (1973)
[4] J. H. Freed, *Annu. Rev. Phys. Chem.* 23, 265 (1972).
[5] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 57, 1004 (1972).
[6] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 58, 2746 (1973). (Hereafter referred to as I.)
[7] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 59, 2869 (1973). (Hereafter referred to as II.)
[8] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 61, 1517 (1974). (Hereafter referred to as III).
[9] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 62, 1790 (1975).

pairs initially in contact first separate and then reencounter, plays a central (but not exclusive) role. The role of this reencounter mechanism was first recognized by Adrian, and the reader is referred to his original papers for a clear and simple introduction to it.[10,11] This work is based heavily on the original papers by the present authors, and the reader is referred to them[5–9,12] for many of the extensive details omitted here.

We present in Section II a detailed exposition of the theoretical approach based upon the SLE. The general properties of the solutions are also discussed. A description of the basic results for the RPM, including the important fundamental relationships and physical interpretations, is given in Section III. Section IV shows how one may introduce improved dynamics into the description and how this both affects the results and amplifies one's understanding. In particular, diffusion under interactive potentials, such as ionic interactions, between radicals is considered. Also, the theoretically important considerations are presented for a self-consistent model in which the spin-dependent exchange interactions affect *both* the time evolution of the spin degrees of freedom *and* the reactive (spin-dependent) diffusion. It should be emphasized here that while the SLE approach is a very general one, the models and interactions considered in detail, while chosen to be the more relevant ones, are still limited for simplicity. In Section V we briefly discuss ways in which they can be extended and improved.

Recently, it has been realized that the RPM is not the only important CIDEP mechanism. Wan and co-workers, in particular, have emphasized the likely importance of initial triplet polarizations when radicals are produced photochemically via intersystem crossing to an excited triplet state.[13,14] An analysis of the orientation-dependent rotating triplet model[15,16] is presented in terms of the appropriate SLE[16] in Section VI.

Finally, in Section VII, we discuss in detail the matter of the observed signal intensities and their time evolution. This section is written in the spirit of the "two-time scale" approach, which is fundamental to much of the analysis in this chapter. That is, the polarization generating process is considered to occur very rapidly compared to other kinetic process (e.g., radical scavenging and individual radical T_1's). Thus, one may solve for the long-time limiting forms of the polarizations, and then incorporate them into more classical type kinetic and magnetization expressions for the time evolution in the

[10] F. J. Adrian, *J. Chem. Phys.* 53, 3374 (1970); 54, 3912 (1971).
[11] F. J. Adrian, *J. Chem. Phys.* 54, 3918 (1971); 57, 5107 (1972)
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[14] J. K. S. Wan, S. K. Wong, and D. A. Hutchinson, *Accounts Chem. Res.* 7, 58 (1974).
[15] P. W. Atkins and G. T. Evans, *Chem. Phys. Lett.* 25, 108 (1974); *Mol. Phys.* 27, 1633 (1974).
[16] J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* 62, 1706 (1975).

slower time scale directly amenable to experiment. The validity of the "two-time scale" approach is discussed at the end of Section III, where it is shown to be usually, but not always, a good approximation.

II. Theoretical Approach

A. Stochastic Liouville Equation

The basic equation describing the spin dynamics of radicals under the combined effects of spin interactions and diffusion in liqiud solution is the stochastic Liouville equation (SLE) given in terms of the spin-density matrix $\rho(\mathbf{r}_l, t)$[4,6]:

$$\frac{\partial \rho(\mathbf{r}_l, t)}{\partial t} = -i\mathscr{H}^{\times}(\mathbf{r}_l)\rho(\mathbf{r}_l, t) + D\Gamma_r \rho(\mathbf{r}_l, t) + \mathscr{K}_r \rho(\mathbf{r}_l, t) \tag{2.1}$$

In this equation $\mathscr{H}^{\times}(\mathbf{r}_l)$ is the Liouville operator associated with the spin Hamiltonian $\mathscr{H}(\mathbf{r}_l)$ (i.e., for any two operators A and B, $A^{\times}B \equiv [A, B]$). We shall consider the interaction of a radical pair A–B, so we may write

$$\mathscr{H}(\mathbf{r}_l) = \mathscr{H}^0(\mathbf{r}_a, \mathbf{r}_b) + \mathscr{H}' \tag{2.2}$$

where $\mathscr{H}^0(\mathbf{r}_a, \mathbf{r}_b)$ is that part of $\mathscr{H}(\mathbf{r}_l)$ which is diagonal in a basis set of coupled electron spins (i.e., singlet–triplet representation). (We use lower case a and b to refer to radicals A and B. Later we specify a and b as particular nuclear configurations of radicals A and B.) It is given by

$$\mathscr{H}^0(\mathbf{r}_a, \mathbf{r}_b) = \tfrac{1}{2}(g_a + g_b)\beta_e \hbar^{-1} B_0 (S_{az} + S_{bz}) + \tfrac{1}{2}\left(\sum_j^a A_j \mathbf{I}_j + \sum_k^b A_k \mathbf{I}_k\right)(\mathbf{S}_a + \mathbf{S}_b)$$
$$- J(\mathbf{r}_a, \mathbf{r}_b)(\tfrac{1}{2} + 2\mathbf{S}_a \cdot \mathbf{S}_b). \tag{2.3}$$

The off-diagonal part, $\mathscr{H}'$ of $\mathscr{H}(\mathbf{r})$ is independent of $\mathbf{r}$ and is given by

$$\mathscr{H}' = \tfrac{1}{2}(g_a - g_b)\beta_e \hbar^{-1} B_0 (S_{az} - S_{bz}) + \tfrac{1}{2}\left(\sum_j^a A_j \mathbf{I}_j - \sum_k^b A_k \mathbf{I}_k\right)(\mathbf{S}_a - \mathbf{S}_b). \tag{2.4}$$

Equation (2.4) expresses the fact that $\mathscr{H}'$ consists only of differences in g-values and hyperfine energies between the two interacting radicals. $J(\mathbf{r}_a, \mathbf{r}_b)$ in Eq. (2.3) is the exchange interaction between radicals A and B, which depends explicitly on $\mathbf{r}_a$, $\mathbf{r}_b$ (or, more precisely, on $\mathbf{r}$ the radial distance between the radicals as well as their relative orientations). We have neglected in Eqs. (2.2)–(2.4) any intramolecular anisotropic g or A tensor contributions, which tend to average out in liquids in times of the order of 10^{-10}–10^{-11} sec. While this is not rigorous, any effects from incomplete averaging should represent

small corrections to the g_a, g_b, A_a, and A_b used in Eqs. (2.3) and (2.4). We also neglect spin-rotational terms, since spin-rotational relaxation is even faster, $\tau_J \lesssim 10^{-12}$ sec. We have also neglected any polarization as well as relaxation due to intermolecular electron–electron dipolar interactions which, like $J(\mathbf{r}_a, \mathbf{r}_b)$, are modulated by the relative translational diffusion of the radicals. In neglecting dipolar interactions, we are guided somewhat by the fact that for free radicals in normal liquids, the exchange mechanism usually predominates in the concentration-dependent spin relaxation. (These interactions can, of course, be explicitly included, if desired, into the very general SLE approach.) We further assume, for simplicity in most cases, that $J(\mathbf{r}_a, \mathbf{r}_b) = J(r)$, i.e., the exchange interaction is independent of the relative molecular orientations and depends only upon radial distance r. Also in the analysis of high-field experiments we need only consider the secular $A_J I_{Jz} S_{az}$-type terms.

The operator $D\Gamma_r$ in Eq. (2.1) is the Markovian operator for the relative diffusion between radicals A and B, i.e., the diffusion in the intermolecular vector $\mathbf{r}$. We first take this to be a normal Brownian diffusion process with diffusion coefficient $D = D_a + D_b$, i.e., the sum of the individual diffusion coefficients. This amounts to neglecting any spin-dependent effects on the diffusive motion, which will be a good assumption when $\hbar|J(r)| \ll kT$. In Section IV, E we explicitly include their effects in order to obtain a self-consistent SLE. The operator $\mathscr{K}$ is introduced as a generalized operator representing the reaction rate constants for the radical pair. It will, in general, be spin dependent. We discuss its general features below.

The diffusion operator Γ_r can be written in spherical polar coordinates in the form:

$$\Gamma_r = \Gamma_r + (1/r^2)\Gamma_\Omega, \tag{2.5}$$

where Γ_r, the radial part, is given by

$$\Gamma_r = (1/r^2)(\partial/\partial r) r^2 (\partial/\partial r), \tag{2.6}$$

while the angular part, Γ_Ω, is

$$\Gamma_\Omega = (1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)] + (1/\sin^2\theta)(\partial^2/\partial\phi^2). \tag{2.7}$$

Our above assumptions effectively allow us to write $\mathscr{H}(\mathbf{r}_a, \mathbf{r}_b) \to \mathscr{H}(\mathbf{r})$, so one may integrate out the angular dependence (of θ and ϕ) in Eq. (2.1), leaving a stochastic Liouville expression for

$$\rho(r, t) = (1/4\pi)\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \rho(\mathbf{r}, t) \tag{2.8}$$

given by

$$\partial\rho(r, t)/\partial t = -i\mathscr{H}^{\times}(r)\rho(r, t) + D\Gamma_r \rho(r, t) + \mathscr{K}_r \rho(r, t), \tag{2.9}$$

where we have also taken $\mathscr{K}_r$ as orientationally independent for simplicity.

The Laplace transform of Eq. (2.9) is

$$s\hat{\rho}(r,s) - \hat{\rho}_0(r) = -i\mathscr{H}^{\times}(r)\hat{\rho}(r,s) + D(\partial^2/\partial r^2)\hat{\rho}(r,s) + \mathscr{K}_r\hat{\rho}(r,s), \tag{2.10}$$

where

$$\hat{\rho}(r,s) \equiv \int_d^\infty e^{-st} r\rho(r,t)\,dt \equiv \int_d^\infty e^{-st}\hat{\rho}(r,t)\,dt \tag{2.11}$$

and $\hat{\rho}_0(r) = r\rho(r,0)$ gives the initial condition and d is the distance of closest approach. Equation (2.10) is an equation in only the single spatial variable r *as well as* in the spins of the radical pair. One could solve Eq. (2.10) by expanding $\hat{\rho}(r,s)$ in eigenfunctions of the diffusion operator (viz., a modified spherical Bessel Function expansion; see Section V, A). However, we have found it more convenient to employ a finite-difference technique. That is, one writes

$$\partial^2\hat{\rho}(r,s)/\partial r^2 = (1/\Delta r^2)[\hat{\rho}(r-\Delta r,s) - 2\hat{\rho}(r,s) + \hat{\rho}(r+\Delta r,s)] \tag{2.12}$$

where Δr is a small but finite increment in r. In principle, one must take Δr small enough to properly represent the functions varying in r. In our case $J(r)$ is the most rapidly varying function of r, and this method allows one to consider a wide range of functional dependences of J with r.

B. Probability Functions and Polarizations

The time-dependent total probability function is defined by

$$\mathscr{P}(t) = \mathrm{Tr}\,\rho(t) \tag{2.13a}$$

and the time-dependent polarization of radical a, or $P_a(t)$, is given by

$$P_a(t) = -2\,\mathrm{Tr}\{\rho(t)S_{az}\} \tag{2.13b}$$

(where the sign convention yields positive equilibrium polarizations P_{eq}), and where

$$\rho(t) \equiv \int_d^\infty r\hat{\rho}(r,t)\,dr. \tag{2.13c}$$

The Laplace transforms of $\mathscr{P}(t)$ and $P_a(t)$ are then given by

$$\mathscr{P}(s) = \mathrm{Tr}\left[\int_d^\infty r\hat{\rho}(r,s)\,dr\right], \tag{2.14a}$$

$$\hat{P}_a(s) = -2\,\mathrm{Tr}\left[\int_d^\infty r\hat{\rho}(r,s)\,dr S_{az}\right]. \tag{2.14b}$$

The quantity $P_a(t)$ is of fundamental importance for CIDEP, while we shall see that the quantity

$$\mathscr{F}(t) \equiv 1 - \mathscr{P}(t)$$

is of fundamental importance for CIDNP. It is easy to see, by writing

$2S_{az} = (S_{az} - S_{bz}) + (S_{az} + S_{bz})$, that the expression Eq. (2.13b) is

$$P_a(t) = -[\rho_{ST_0}(t) + \rho_{T_0S}(t)] + [\rho_{T_-T_-}(t) - \rho_{T_+T_+}(t)] \tag{2.15a}$$

while

$$P_b(t) = +[\rho_{ST_0}(t) + \rho_{T_0S}(t)] + [\rho_{T_-T_-}(t) - \rho_{T_+T_+}(t)]. \tag{2.15b}$$

Also

$$\mathscr{P}(t) = \rho_{SS}(t) + \rho_{T_0T_0}(t) + \rho_{T_+T_+}(t) + \rho_{T_-T_-}(t). \tag{2.15c}$$

In Eqs. (2.15) S, T_0, and $T_\pm$ refer to the standard singlet and triplet states of the radical pair, while ρ_{AB} refers to the ABth matrix element of ρ. One notes from Eqs. (2.15) that the first bracketed terms yield opposite CIDEP polarizations for radicals a and b, while the second bracketed terms give identical polarizations. In the high-field approximation the form of Eq. (2.4) means that only S and T_0 states couple to give induced polarizations, while $T_\pm$ states remain unchanged except when the initial triplet polarization is operative (cf. Section VI). Thus for the high-field radical-pair mechanism we can neglect the $\rho_{T_\pm T_\pm}(t)$ in Eqs. (2.15).

We note that while most of our analysis is given in the $S, T_0, T_\pm$ representation, it is often useful to interconvert between density-matrix elements in that representation and those in the product representation of doublet pairs, which we write as $\rho_{+a,-b;+a-b} = \rho_{+a-b}$; $\rho_{+a,-b;-a+b}$, etc. The relationships are easily obtained in the usual way for matrix transformations, and we give the important ones here for convenience:

$$\begin{aligned}
\rho_{T\pm,T\pm} &= \rho_{a\pm,b\pm}\\
\rho_{T_0,T_0} &= \tfrac{1}{2}(\rho_{+a,-b} + \rho_{-a,+b}) + \mathrm{Re}\,\rho_{+a-b;-a+b}\\
\rho_{S,S} &= \tfrac{1}{2}(\rho_{+a,-b} + \rho_{-a,+b}) - \mathrm{Re}\,\rho_{+a,-b;-a+b}\\
\rho_{S,T_0} &= \tfrac{1}{2}(\rho_{+a,-b} - \rho_{-a,+b}) + i\,\mathrm{Im}\,\rho_{+a,-b;-a,+b}.
\end{aligned}$$

Also:

$$\begin{aligned}
\rho_{\pm a,\mp b} &= \tfrac{1}{2}(\rho_{S,S} + \rho_{T_0,T_0}) \pm \mathrm{Re}\,\rho_{S,T_0}\\
\rho_{+a,-b;-a,+b} &= \tfrac{1}{2}(\rho_{T_0,T_0} - \rho_{S,S}) + i\,\mathrm{Im}\,\rho_{S,T_0}.
\end{aligned}$$

One notes that the initial condition must be specified to solve Eq. (2.10). The precise initial condition one utilizes depends on the specific physical model appropriate to the experiment. Thus, for example, one may have a chemical reaction which produces radical pairs initially in pure singlet (or pure triplet) states. Then the stochastic Liouville equation (2.9) or (2.10) is solved subject to this initial condition, e.g., $\rho_0(r)_{SS} = \delta(r-r_0)/r_0^2$ where r_0 is the initial separation. Alternatively, the polarization may be conceived of as being generated whenever independently produced radicals approach one another and have a finite probability of reacting. The initial conditions here would then involve equal populations in the S and T_0 states, which is a direct consequence of (1) having equal initial populations of states $+a, -b$ and

$-a, +b$ and (2) having random initial phases, i.e., $\rho_{\pm a, \mp b, \mp a \pm b}(t=0) = 0$, etc. Thus, the probability and polarization transforms $\bar{\mathscr{P}}(s)$ and $\bar{P}_a(s)$ may be obtained from Eqs. (2.10), (2.11), (2.14), and Laplace transform of Eqs. (2.15) once the appropriate initial conditions are chosen. Then $\mathscr{P}(t)$ and $P_a(t)$ are recovered by inverse transformation. However, we will find that we need just the limiting values of $\mathscr{P}(t)$ and $P_a(t)$ as $t \to \infty$, which are

$$\mathscr{P} \equiv \lim_{t\to\infty} \mathscr{P}(t) = \lim_{s\to 0} s\bar{\mathscr{P}}(s) \tag{2.16a}$$

and

$$P_a^{\infty} \equiv \lim_{t\to\infty} P_a(t) = \lim_{s\to 0} s\bar{P}_a(s). \tag{2.16b}$$

In the high-field approximation, when the $T_{\pm}$ states do not contribute to the induced polarization, one has

$$P_a^{\infty} = -2 \lim_{s\to 0} s \int_d^{\infty} r \,\mathrm{Re}[\bar{\rho}_{ST_0}(r,s)]\, dr \tag{2.17a}$$

and we neglect the contributions of the $T_{\pm}$ states in obtaining $\mathscr{P}$ as

$$\mathscr{P} = \lim_{s\to 0} s \int_d^{\infty} r[\bar{\rho}_{SS}(r,s) + \bar{\rho}_{T_0T_0}(r,s)]\, dr. \tag{2.17b}$$

We also have the quantity

$$\mathscr{F} \equiv 1 - \mathscr{P} \tag{2.17c}$$

which is the total fraction of radicals that react.

C. Stochastic Matrix and Boundary Conditions

The application of the finite difference technique, expressed by Eq. (2.12), is essentially equivalent to transforming the continuous diffusion equation (a Fokker–Planck equation) into a discrete Master equation involving a transition-probability matrix W, coupling $\rho(r,t)$ between discrete values $\rho(r_0 + j\Delta r, t)$ where $j = 0, 1, 2, \ldots, N$. These discrete values form a column vector $\boldsymbol{\rho}$. Thus

$$D\,\partial^2\rho/\partial r^2 \to \mathbf{W}\boldsymbol{\rho}. \tag{2.18}$$

If we let $r_0 = d$ be the distance of closest approach, and if we do not allow any net accumulation of radicals at this point, then this establishes a boundary condition, which is formally equivalent to a reflecting wall. This condition is

$$\partial\rho(r,t)/\partial r]_{r=d} = 0 \tag{2.19}$$

or, equivalently,

$$\partial\bar{\rho}(r,s)/\partial r]_{r=d} - \bar{\rho}(d,s)/d = 0. \tag{2.19a}$$

In finite difference notation, Eq. (2.19a) becomes

$$\{[\bar{\rho}(d+\Delta r, s) - \bar{\rho}(d-\Delta r, s)]/2\Delta r\} - [\bar{\rho}(d,s)/d] = 0. \tag{2.19b}$$

Then for $r = d$, Eq. (2.12) gives

$$D\,\partial^2\bar{\rho}(r,s)/\partial r^2]_{r=d} \to (D/\Delta r^2)\{-2[1+(\Delta r/d)]\,\bar{\rho}(d,s) + 2\bar{\rho}(d+\Delta r, s)\} \tag{2.20}$$

where we have now eliminated the $\rho(d-\Delta r)$ term.

In order to make the calculation tractable, one must limit the space to a finite region, the outer limit of which is given by $r_N = r_0 + N\Delta r$. A choice of the value of r_N is guided by two considerations: (1) it must be large enough that particles separated by r_N exert no exchange interaction, i.e., $J(r_N) = 0$; (2) the probability $t_{N,K}$ must be small enough that particles separated by r_N will diffuse close enough (i.e., to r_K) such that $J(r_K) \approx Q$. One has $t_{N,K} = r_K/r_N$.[17] This second condition is needed to permit reencounters of the radical pair. It is clear that a reflecting barrier at r_N would induce physically unjustified extra encounters (especially as $t \to \infty$), so an absorbing wall, or more precisely a collecting wall, is required. Thus, as $t \to \infty$, the radical pair achieves unit probability of being separated by $r_N \gg r_0$.

We now adopt the notation of writing $\bar{\rho}(r_0 + j\Delta r, s)$ as $\bar{\rho}(j,s)$ and a transition-probability matrix element of W in Eq. (2.18) such as $W_{r_0+j\Delta r \to r_0+k\Delta r}$ as $W_{k,j}$. Then the collection condition at $r = r_N$ is

$$W_{N,N} = W_{N-1,N} = 0, \tag{2.21}$$

i.e., the radical pairs collect at r_N and cannot diffuse back. The total W is then given as a tridiagonal matrix:

$$\frac{D}{\Delta r^2}\begin{pmatrix} -2[1+(\Delta r/d)] & +2 & & & & & \\ 1 & -2 & 1 & & & & \\ & 1 & -2 & 1 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & 1 & -2 & 1 & \\ & & & & 1 & -2 & 0 \\ & & & & & 2 & 0 \end{pmatrix} \tag{2.22}$$

where the last row has been determined by the conservation of total probability requirement (see below), which is slightly different from a reflecting wall condition such as Eq. (2.20), but more desirable for convergence.

[17] J. M. Deutch, *J. Chem. Phys.* 56, 6076 (1972).

Note now that in the finite difference technique we approximate the integral in Eqs. (2.14) for $\hat{\mathcal{P}}(s)$ and $\hat{P}_0(s)$ as

$$\int_d^\infty r\hat{p}(r,s)\,dr = \sum_{i=0}^{N} V(i)\,\hat{p}(i,s), \tag{2.23}$$

where $V(i)$ is the radial weighting factor for the r_ith position. Specifically one has

$$\begin{aligned} V(0) &= d\Delta r/2, \\ V(i) &= r_i\Delta r, \qquad \text{for} \quad 0 < i < N. \\ V(N) &= r_N\Delta r/2, \end{aligned} \tag{2.24}$$

Now the diffusion equation in the absence of spin-dependent phenomena is, of course,

$$d\hat{p}(r,t)/dt = D\Gamma_r\hat{p}(r,t) \rightarrow \mathrm{W}\hat{p}(r,t) \tag{2.25}$$

where $\hat{p}(r,t) = rp(r,t)$, and $p(r,t)$ is the classical probability density. The arrow in Eq. (2.25) just reflects the passage to a finite difference expression [cf. Eq. (2.18)]. Then the conservation of probability condition is[18]

$$\sum_{i=0}^{N} V(i)W_{i,j} = 0, \qquad \text{for} \quad j = 0, 1, \ldots, N. \tag{2.26}$$

That is, the weighted sum of elements of W for each column must be zero. The W matrix given by Eq. (2.22) is seen to be in accordance with Eq. (2.26).

There is a convenient way of keeping r_N large enough to satisfy the above two conditions, while having Δr small enough to converge to the correct solution, and yet keep N from getting too large. In the region where $J(r) \neq 0$ one has $r_0 \leqslant r \leqslant r_M$ with $r_M \ll r_N$. In this region Δr must be chosen small enough compared to the variation in $J(r)$. However, for $r_M \leqslant r \leqslant r_N$, where $J(r) = 0$, Δr can be taken much larger and still adequately describe just the Brownian diffusion. We take the Δr in the latter region as f times larger than that of the former region (where $f \sim 10$ to 100). Then Eqs. (2.24) become

$$\begin{aligned} V(0) &= \mathrm{d}\Delta r/2, \\ V(i) &= r_i\Delta r, \qquad \text{for} \quad 0 < i < M, \\ V(M) &= r_M(1+f)\,\Delta r/2, \\ V(i) &= r_i f\Delta r, \qquad \text{for} \quad M < i < N. \\ V(N) &= r_N f\Delta r/2, \end{aligned} \tag{2.27}$$

The matrix elements of W are again given as in Eq. (2.22) for $r_i < r_M$. For $r_i > r_M$ they can be obtained from the elements of Eq. (2.22) by dividing by f^2. The Mth row is determined by the conservation of probability [Eqs. (2.26)] with the $V(i)$'s of Eq. (2.27). One finds

$$\begin{aligned} W_{M,M-1} &= [2/(1+f)](D/\Delta r^2), \\ W_{M,M} &= -(2/f)(D/\Delta r^2), \\ W_{M,M+1} &= [2/(1+f)f](D/\Delta r^2). \end{aligned} \tag{2.28}$$

[18] J. B. Pedersen, *in* "Electron-Spin Relaxation in Liquids" (L. T. Muus and P. W. Atkins, eds.), Chapter III. Plenum, New York, 1972.

D. The Matrix Solution

One now needs the matrix elements of $\mathscr{H}(r)^\times\rho$. These are obtained utilizing Eqs. (2.2)–(2.4). One finds that

$$\mathscr{H}^\times(S,T_0) = \begin{array}{c} \begin{matrix} SS & ST_0 & T_0S & T_0T_0 \end{matrix} \\ \begin{pmatrix} 0 & -Q & Q & 0 \\ -Q & 2J(r) & 0 & Q \\ Q & 0 & -2J(r) & -Q \\ 0 & Q & -Q & 0 \end{pmatrix} \end{array} \tag{2.29}$$

for the subspace defined by the S and T_0 levels. In the high-field approximation this subspace does not couple to the remainder of the 16×16 dimensional space needed for a complete representation of $\mathscr{H}^\times$. Furthermore, in this approximation $[\mathscr{H}^\times\rho]_{T_+T_+} = [\mathscr{H}^\times\rho]_{T_-T_-} = 0$, so the $T_\pm$ states cannot contribute to the polarization process. Note that in Eq. (2.29)

$$2Q \equiv (g_a - g_b)\beta_e\hbar^{-1}B_0 + \left(\sum_j^a A_j^a M_j^a - \sum_k^b A_k^b M_k^b\right) \tag{2.30}$$

so $2Q$ is the difference in ESR resonant frequencies between radicals A and B (when $J = 0$). Actually Eqs. (2.29) and (2.30) imply a particular configuration of nuclear spin states in the two radicals labeled a and b, so this is sufficiently general for considering the interaction of an arbitrary radical pair.

One easily finds, by transforming the matrix of Eq. (2.29) to a representation of $\rho_\pm \equiv (2)^{-1/2}(\rho_{S,S} \pm \rho_{T_0,T_0})$ instead of $\rho_{S,S}$, $\rho_{T,T}$, etc., that $[\mathscr{H}^\times\rho]_{+,+} = 0$, which just expresses the conservation of spin in the reduced four-dimensional subspace. In the absence of spin-selective chemical reactions which destroy radicals, this can be used to convert the needed subspace to just three dimensions.

The complete solution given by Eq. (2.10) now becomes a matrix equation:

$$[s\mathbf{1} - \mathbf{K}' - \mathbf{W}' + i\boldsymbol{\Omega}]\hat{\boldsymbol{\rho}}(s) = \hat{\boldsymbol{\rho}}(0) \tag{2.31}$$

such that the vector space in which $\boldsymbol{\rho}(s)$ is defined is the $4(N+1)$-dimensional space formed from the direct product of the four-dimensional spin-space of

Eq. (2.29) and the $(N+1)$-dimensional space of Eq. (2.22). The Ω in Eq. (2.31) is block-diagonal, where each block is given by Eq. (2.29) for the particular value of r. The W' in Eq. (2.31) is just the W matrix of Eq. (2.22) [as modified according to Eq. (2.28) and the associated discussion], but with each element replaced by the product of that element and a 4×4 unit matrix, since $D\Gamma_r$ is independent of spin. The K' matrix is the appropriate form of the $\mathscr{K}_r$ operator as discussed below.

One solves the matrix Eq. (2.31) for the elements of $\hat{\rho}(s)$ or $\hat{\rho}(i,s)$ and then the total final probability Φ is given from Eq. (2.17b):

$$\Phi = \lim_{s\to 0} s \sum_{i=0}^{N} V(i)\,[\hat{\rho}_{S,S}(i,s)+\hat{\rho}_{T_0T_0}(i,s)] \tag{2.32}$$

since, as already noted, we normalize to unity only in terms of S and T_0 states, neglecting the unimportant $T_\pm$ states. When $\mathbf{K}=0$, then there is conservation of total probability

$$\Phi(s) = \sum_{i=0}^{N} V(i)\,[\hat{\rho}_{S,S}(i,s)+\hat{\rho}_{T_0T_0}(i,s)] = 1/s. \tag{2.32a}$$

Similarly the polarization of radical a is given, from Eq. (2.17), by

$$P_a^{\infty} = -2\lim_{s\to 0} s \sum_{i=0}^{N} V(i)\,\mathrm{Re}[\hat{\rho}_{ST_0}(i,s)]. \tag{2.33}$$

The vector $\hat{\rho}(0)$ in Eq. (2.31) consists of the initial conditions. One can anticipate a variety of initial conditions, but since Eq. (2.21) is linear and homogeneous in $\rho(r,t)$, then one is free to superpose solutions for the simplest forms of initial conditions to obtain solutions for more complex initial conditions.

E. General Comments, $\mathscr{K}=0$, CIDEP

If $\mathbf{K}'=0$ in Eq. (2.31), then initial conditions must be chosen to yield a net excess of triplets or singlets. We show this by first rewriting Eq. (2.29) in a coupled basis set as:

$$\mathscr{K}(S,T_0)^{\times}\rho = (1/2^{1/2})\begin{pmatrix} 0 & J & Q \\ J & 0 & -Q \\ 0 & -Q & 0 \end{pmatrix}\begin{pmatrix} \rho_{S,T_0}+\rho_{T_0,S} \\ \rho_{S,T_0}-\rho_{T_0,S} \\ \rho_S-\rho_{T_0} \end{pmatrix}. \tag{2.34}$$

The term in $(\rho_S+\rho_{T_0})$ is uncoupled as already noted. It is clear then that the initial condition $\rho(0)$ in the same basis as Eq. (2.34) is, for pure triplets, thus seen to be just minus that for pure singlets [note $\rho_{S,T_0}(i,t=0)=0$] provided, of course, the initial spatial distributions are the same. The superposition property of the solution to Eq. (2.1) then means that $P_a(t)$ given by Eq. (2.15a) (recalling that $T_\pm$ states do not contribute) only changes in sign. Any mixture of S and T_0 initial states then follows from the superposition. Thus an initial random distribution of singlets and triplets cannot give any polarization.

By similar arguments to that just given, one finds from the form of Eqs. (2.31) and (2.34) that the effect of letting $Q\to -Q$ is equivalent to changing the sign of the polarization provided the initial condition is just some admixture of singlet and triplet states [with no initial polarization, i.e., $\rho_{S,T}(i,t=0)=0$]. [Similar conclusions may be obtained from Eqs. (2.15) and (2.30) for the definition of Q.] The effect of changing $J\to -J$ is also seen, from Eq. (2.34), to result in a reversal in sign of the polarization [provided $\rho_{S,T}(i,t=0)=0$].

One can further show that, even for pure singlet initially, a uniform spatial distribution of radical pairs will not yield any polarization. In particular, this means that there must be some initial preferential close separation of the radical pair, as would naturally occur when the radical pair forms from the cleavage of a parent molecule. We usually consider the case of pure singlet (or pure triplet) at $r_0=d$ for which

$$\hat{\rho}_{S,S}(i,t=0) = \delta_{i,0}/V(0). \tag{2.35}$$

Thus the CIDEP polarization process may be thought of as follows. Suppose a radical pair in the T_0 state initially formed from a cleavage. Then from Eq. (2.34) one obtains $\mathrm{Re}\,\rho_{S,T_0}$, required in Eq. (2.17), in two (quantum-mechanically coherent) steps. First there is a singlet–triplet mixing which we shall refer to as "Q-mixing," i.e.,

$$\rho_{T_0} \overset{Q}{\rightleftharpoons} \rho_{S,T_0}-\rho_{T_0,S}. \tag{2.36a}$$

Then the process is completed by the effects of $J(r)$ when the radicals are close enough:

$$\rho_{S,T_0}-\rho_{T_0,S} \overset{J(r)}{\rightleftharpoons} \rho_{S,T_0}+\rho_{T_0,S}. \tag{2.36b}$$

As will be shown later, this is primarily due to reencounters of the radical pair. These polarization generating steps are the same as those originally proposed by Adrian.[10,11]

F. General Comments, $\mathscr{K}\neq 0$

1. *CIDEP*

One conclusion of Section II, D was that no CIDEP polarization could be created unless there was an excess of singlets or triplets. When two independently produced radicals happen to collide, then there will be equal probabilities of forming a singlet or each of the triplet states, and as a result

no polarization. This situation however, is changed if the radicals can react via a selective chemical reaction, i.e., the probability for a reaction is higher for singlets than for triplets (or vice versa). Such a selective reaction will have the effect of eliminating some singlets at the first encounter leaving a net triplet character. The situation is now similar to what we have previously considered. Therefore the polarization process may now begin. We will follow the usual approach, by assuming that the probability for reaction is proportional to the singlet character of the colliding radicals and also that the radicals have to be within a certain distance to react, i.e., the "sphere of influence." Thus we define a "first-order chemical rate constant" $k(r)$, which gives the probability of the radical pair of singlet character reacting per unit time as a function of the interradical separation r. It is necessary to introduce this "rate constant" into a now nonzero K' matrix to allow for the disappearance of singlet (or triplet) at the first encounter as well as *all* subsequent radical-pair encounters. One may use a variety of forms for the functional dependence of $k(r)$ on r. We usually utilize the simple form:

$$k(r_l) = k\delta_{l,0} \tag{2.37}$$

so the "sphere of influence" is just d to $d+\Delta r_k$ with $\Delta r_k = \Delta r$.

We then may take as our initial condition the instant when the radical pair first approaches the minimum separation d, since no polarization can have been built up previously for random-initial singlet and triplet character. Thus, our solutions based on Eq. (2.33) just give the total polarization developed per radical-pair "collision," where by a single collision we include the first encounter and *all* reencounters of the radical pair before it finally diffuses away. This polarization also includes the effect of the chemical reaction in depleting the total number of radicals.

2. *CIDNP*

In general, observable CIDNP effects require the existence of a spin-selective chemical reaction for the radical pair. In particular, one observes the effect of the Q-mixing on the reactivity of the radical pair. Thus, suppose there is a singlet reaction given by Eq. (2.37) and initially the radical pair is formed in the T_0 state. Then, from Eq. (2.34) one notes that ρ_{SS}, which can then react, is generated in two (quantum mechanically coherent) steps via "Q-mixing" or singlet–triplet mixing:

$$\rho_{T_0} \overset{Q}{\rightleftharpoons} \rho_{S,T_0} - \rho_{T,S} \overset{Q}{\rightleftharpoons} \rho_S - \rho_{T_0}. \tag{2.38}$$

In general, we shall find that the Q-mixing is effective as the radical pair separate, and a reaction will occur when the radicals reencounter.

The CIDNP phenomenon is best discussed in terms of the quantity $\mathscr{F} - \mathscr{F}_0$, where $\mathscr{F}_0$ is the value of $\mathscr{F}$ calculated for $Q = 0$, i.e., it excludes any effects

from singlet–triplet (S–T_0) mixing. Thus $\mathscr{F} - \mathscr{F}_0$ specifically gives the extra probability of reaction due to the S–T_0 mixing.

We calculate separate results for singlet (S) initial, triplet (T_0) initial, and random-initial (R.I.) precursors (equal amounts of S and T_0). All other cases are obtained as simple superpositions of these. (Of course, R.I. is a superposition of S and T_0 also.) We indicate results for $\mathscr{F}$, etc., as $\mathscr{F}(S)$, $\mathscr{F}(T_0)$, etc., to indicate the particular initial condition utilized.

One should note from our discussion given here, as well as the definition of Eq. (2.17c), that $\mathscr{F}$ has the very important physical meaning of the probability that the radical pair reacts per collision, where by a collision we again mean the first encounter as well as all possible reencounters before the radicals finally diffuse away. Also $\mathscr{P}$ is the probability that the radical pair will survive the collision without reacting.

Similarly, for CIDEP one may define a normalized polarization $P_a^{\infty}/\mathscr{P}$ which gives the correct polarization for the radicals that survive the collision. However, it will be shown in Section VII that the quantity most directly related to experimental results is $P_a^{\infty}/\mathscr{F}$.

G. Forms of $\mathscr{K}(r)$ and $J(r)$

There still remains a fundamental question as to the spin-dependent form of the superoperator $\mathscr{K}$. A sensible choice is

$$\mathscr{K}\rho = [-k(r)/2][|S\rangle\langle S|\rho + \rho|S\rangle\langle S|] \equiv [-k(r)/2]|S\rangle\langle S|^{+}\rho \tag{2.39}$$

which implies $\rho_{SS}(d)$ decays with rate constant $k(d)$ while $\rho_{S,T_0}(d)$ and $\rho_{T_0,S}(d)$ decay with rate $k(d)/2$. That is, the off-diagonal density matrix elements $\rho_{ST_0}(d)$ and $\rho_{T_0S}(d)$ should also decay by a Heisenberg uncertainty in lifetime effect given as the mean of the decay rate of S and T_0 states.

However, the self-consistent analysis, including spin dependence of the diffusion process (cf. Section IV, E), indicates that a more satisfactory representation of $\mathscr{K}$ is given by

$$\mathscr{K}\rho = -k(r)|S\rangle\rho_{SS}\langle S|, \tag{2.40}$$

i.e., only the diagonal element $\rho_{SS}(d)$ decays. This matter will be discussed further in Section IV, and we shall favor the latter form, Eq. (2.40), in our analysis. Also, this form leads to physically more easily interpretable results.

We usually employ an exponentially decaying exchange interaction

$$J(r) = J_0 e^{-\lambda(r-d)} \tag{2.41}$$

with $r_{ex} \equiv \lambda^{-1} 5 \ln 10$ giving the range over which $J(r)$ decays to 10^{-5} its initial value. This form of $J(r)$ is expected from valence calculations, and one usually expects that r_{ex} will be of the same order of magnitude as d.

H. Dimensionless Variables

One may transform Eq. (2.9) into dimensionless form subject to the reflecting wall boundary condition at $r_0 = d$ by introducing

$$\Phi(x,\tau) \equiv (r/d)\rho(r,t) = (1+x)\rho(r,t) \tag{2.42}$$

with dimensionless variables $x = r/d-1$ and $\tau = Dt/d^2$. Then Eq. (2.10) becomes

$$\sigma\Phi(x,\sigma) - \Phi_0(x) = [-l(d^2/D)\mathscr{H}^x(x)+(\partial^2/\partial x^2)+(d^2/D)\mathscr{K}_r]\Phi(x,\sigma) \tag{2.43}$$

where

$$\rho(t) = \int_0^\infty d^3(x+1)\Phi(x,\tau)\,dx \tag{2.44}$$

and

$$\Phi(x,\sigma) \equiv \int_0^\infty \Phi(x,\tau)e^{-\tau\sigma}\,d\sigma \tag{2.45}$$

with $\sigma = d^2s/D$. The relevant independent dimensionless variables for P_s^∞, $\mathscr{P}$, and $\mathscr{F}$ then become: $J_0 d^2/D$, Qd^2/D, kd^2/D, r_{ss}/d [or $(\lambda d)^{-1}$], and $\Delta r_k/d$ (also $\hbar J_0/kT$ and $\Delta r/d$).

III. Basic Results for the Radical-Pair Mechanism

A. CIDNP

Our numerical results (where at $t=0$ the particles are in contact) may be summarized by a series of relatively simple expressions.[8] First define

$$\Lambda \equiv \mathscr{F}_0(S) \tag{3.1}$$

and

$$\mathscr{F}^* \equiv \lim_{\Lambda\to 1}\mathscr{F}(T_0) = \lim_{\Lambda\to 1}[\mathscr{F}(T_0)-\mathscr{F}_0(T_0)]. \tag{3.2}$$

Thus Λ is *precisely* the fractional probability of reaction (for $Q=0$) of singlets for the whole "collision" including all reencounters, while $\mathscr{F}^*$ measures the conversion from triplets to singlets for the whole collision. Then one obtains from the numerical solutions the *exact* relation:

$$-[\mathscr{F}(S)-\mathscr{F}_0(S)] = -[\mathscr{F}(S)-\Lambda] = +(1-\Lambda)\mathscr{F}(T_0). \tag{3.3}$$

Equation (3.3) shows that the net decrease in reaction for pure singlets per collision due to $Q \neq 0$ is just the probability a singlet does not react for $Q = 0$ (i.e., $1-\Lambda$) times the probability pure triplets do ultimately react because of Q-mixing. The factor $(1-\Lambda)$ corrects for the fact that if singlets react fast, then they are not available to be converted to triplets by Q-mixing.

If one now uses the superposition principle to write

$$\mathscr{F}(\text{R.I.}) = \tfrac{1}{2}[\mathscr{F}(S)+\mathscr{F}(T_0)], \tag{3.4}$$

then Eq. (3.3) may be rewritten as

$$[\mathscr{F}(\text{R.I.})-\mathscr{F}_0(\text{R.I.})]/\mathscr{F}_0(\text{R.I.}) = \mathscr{F}(T_0). \tag{3.5}$$

The physically important parameter Λ is found[8] to obey the simple relation

$$\Lambda = k\tau_1/(1+k\tau_1). \tag{3.6}$$

For Eq. (2.37), where the "sphere of influence" of $k(r)$ extends from d to $d+\Delta r_k$, one obtains

$$\tau_1 = d\Delta r_k/D, \tag{3.7}$$

where τ_1 is a characteristic lifetime of the interacting pair. One may rewrite $\tau_1^{-1} \simeq 4\pi Dd/\Delta V$ where ΔV is the "reaction volume" in accordance with earlier theories for lifetimes of reacting pairs.[19] These theories arbitrarily define ΔV as the total volume swept by the interacting pair: $(4/3)\pi d^3$, but our results show that $\Delta V \simeq 4\pi d^2\Delta r_k$, the annular volume of the "contact region." This is precisely the annular volume in the finite difference approximation. By letting k range over several increments in Δr, we have found that Eq. (3.6) still holds, and a more appropriate definition for particles initially in contact is

$$k\tau_1 \equiv D^{-1}\int_d^{d+\Delta r_k} rk(r)\,dr \to D^{-1}\sum_{i=0}^{n=(\Delta r_k/\Delta r-\frac{1}{2})} V(i)\,k(r_i) \tag{3.7'}$$

where $V(i) = r_i\Delta r$ for $i > 0$ (and $\frac{1}{2}d\Delta r$ for $i=0$); cf. Eq. (2.24). The arrow in Eq. (3.7') implies conversion to the finite difference form. This lifetime τ_1, it is clear, is to be interpreted as the effective time for reaction for the whole "collision" and not just for the single encounter of a pair of particles initially in contact.

Actually, it is the dimensionless product $k\tau_1$ (or Λ) which represents a fundamental observable. Thus, by comparison with typical treatments of diffusive effects on reaction-rate constants,[19,20] one has that k_f, the experimentally observed rate constant including the effect of diffusion but assuming steady state fluxes, is given by

$$k_f = \Lambda 2k_2(d) \tag{3.8}$$

where $2k_2(d) = 4\pi dD$ is the rate of new bimolecular encounters. When $k\tau \ll 1$, then $\Lambda \simeq k\tau_1$ and Eq. (3.8) assumes the form appropriate when the relative diffusion is able to maintain equilibrium probability distributions in r, since the reaction is very slow.[19,20]

[19] E.g., I. Amdur and G. G. Hammes, "Chemical Kinetics," Chapter 2. McGraw-Hill, New York, 1966.

[20] R. M. Noyes, *Progr. React. Kinet.* 1, 129 (1961).

The role of the parameter $\mathcal{F}^*$ is seen in the following relation:

$$\mathcal{F}(T_0) = \Lambda\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1} \tag{3.9a}$$

which, by Eq. (3.3), becomes

$$-[\mathcal{F}(S)-\Lambda] = \Lambda(1-\Lambda)\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1} \tag{3.9b}$$

and by superposition:

$$[\mathcal{F}(\text{R.I.})-\mathcal{F}_0(\text{R.I.})] = \tfrac{1}{2}\Lambda^2\mathcal{F}^*[1+\mathcal{F}^*(1-\Lambda)]^{-1}. \tag{3.9c}$$

An approximate form of Eq. (3.9a), viz., $\mathcal{F}(T_0) \simeq \mathcal{F}^*\Lambda$, which becomes Eq. (3.9a) as $\Lambda \to 1$, may be interpreted to mean that the probability of reaction for initially triplet radical pairs equals the probability that triplets are converted to singlets ($\mathcal{F}^*$) multiplied by the probability that the singlets react (Λ).

The factor $[1+\mathcal{F}^*(1-\Lambda)]^{-1}$ may be understood in terms of its infinite series expansion $\sum_{r=0}^{\infty}(-)^r\mathcal{F}^{*r}(1-\Lambda)^r$, where, for example, the $r=1$ term $\mathcal{F}^*(1-\Lambda)$ corrects for the fact that some initially triplet radical pairs, which would first be converted to singlet by Q-mixing and then reencounter and react with certainty if $\Lambda = 1$, would, for $\Lambda < 1$, not react and be converted back to triplet for subsequent encounters. (Note that $\mathcal{F}^*$ by dynamic reversibility in quantum mechanics measures conversion from singlets to triplets and *vice versa* for a "collision.") The higher order corrections along these lines appear as the other terms in the series.

When the initial separation $r_1 > d$, then we have found that Eqs. (3.9) may be modified as follows:

$$\Delta\mathcal{F}(\text{R.I.}\, r_1)/\Delta\mathcal{F}(\text{R.I.}, d) = t_f \tag{3.10}$$

where $\Delta\mathcal{F}(\text{R.I.}\, r_1) = \mathcal{F}(\text{R.I.})-\mathcal{F}_0(\text{R.I.})$ with initial separation of r_1, and t_f is the transfer factor, which for a simple diffusive model is simply

$$t_f = d/r_1 \tag{3.10a}$$

and is just the reencounter probability (i.e., $1-t_f$ is the total probability that two particles initially separated by r_1 will never encounter at $r=d$) discussed originally by Noyes[20] and obtained for continuous diffusion by Deutch.[17] Equation (3.10) is seen to be a simple consequence of the fact that for random initial condition, the CIDNP process only starts upon initial encounter. The result for triplet initial is

$$\mathcal{F}(T, r_1)/\mathcal{F}(T, d) = 1-\chi \tag{3.11}$$

where χ is usually a small quantity $\leqslant 0.1$ (but it becomes more significant in viscous media). It corrects for the fact that some of the triplets are converted to singlets before the first encounter. We have found that, for $r_1 \sim 2d$, it may be approximated by

$$\chi \simeq t_f'^2(1-t_f')\mathcal{F}^*/[1+(1-t_f')\mathcal{F}^*] \tag{3.11a}$$

with $t_f' = r^*/r_1$ for $r_1 \geqslant r^*$ (but if $r_1 \leqslant r^*$ then $t_f' = 1$ and there is no correction), and r^* is defined by $J(r^*) \simeq Q/5$ [where the dependence upon $J(r)$ is a type of excluded volume effect discussed below]. It follows from Eqs. (3.10), (3.11), and (3.5) that

$$\Delta\mathcal{F}(S, r_1)/\Delta\mathcal{F}(S, d) = [1-\chi-\Lambda t_f]/[1-\Lambda]. \tag{3.12}$$

In the case where $r_1 \gg d$, then one may apply Eq. (3.10) independently of the initial condition, since the Q-mixing will tend to equalize any initial unequal S–T_0 distribution.

Given the above relations, then, it is only necessary to determine $\mathcal{F}^*$ in order to obtain the CIDNP polarizations for a given Λ and initial set of conditions. We have found that over much of the range of the relevant parameters, $\mathcal{F}^*$ obeys essentially a $Q^{1/2}$ dependence, as first predicted by Adrian.[10] This is clearly a result of the reencounter phenomenon. However, as Qd^2/D becomes large, a weaker dependence upon Q than the $\frac{1}{2}$ power is observed. This reflects the reduced importance of reencounters, with the S–T_0 mixing becoming optimal for all Q values. In the case of $J_0 d/\lambda D < 1$, the results for $\mathcal{F}^*$ are independent of $J(r)$, and one then obtains for small $J_0 d^2/D$

$$\mathcal{F}^* \simeq [Qd^2/D]^{1/2}/[2+\tfrac{1}{2}(Qd^2/D)^{1/2}]. \tag{3.13}$$

This result shows that (1) the relevant "diffusive length" is d when (a) the

TABLE I[a]

DEPENDENCE OF $\mathcal{F}^*$ UPON $J(r)$[b,c]

J_0	D = 10^{-6} r_{ex} = 2 Å	$D = 10^{-6}$ r_{ex} = 4 Å	$D = 10^{-6}$ r_{ex} = 8 Å	$D = 10^{-5}$ r_{ex} = 8 Å	$D = 10^{-4}$ r_{ex} = 8 Å
10^8	1.0	1.0	1.0	1.0	1.0
10^9	0.997	0.990	0.961	1.0	1.0
10^{10}	0.872	0.782	0.691	0.957	1.0
10^{11}	0.800	0.711	0.595	0.800	0.977
10^{12}	0.781	0.646	0.510	0.745	0.910
10^{13}	0.756	0.592	0.447	0.687	0.886
10^{14}	0.733	0.546	0.391	0.636	0.859
10^{15}	0.712	0.508	0.328	0.589	0.833

[a] From Pedersen and Freed,[8] by permission.

[b] EFA Model. Results given as the ratio $\mathcal{F}^*/\mathcal{F}^*_{J_0=0}$ where $\mathcal{F}^*_{J_0=0}$ is the value obtained for $J_0 = 0$.

[c] Parameters used. $d = 4$ Å, $\Delta r = 0.25$ Å, $f = 20$, $M = 40$, $N = 208$, $r_N = 854$ Å, $Q = 4\times10^8$ sec^{-1}, $k = 10^{10}$ sec^{-1}.

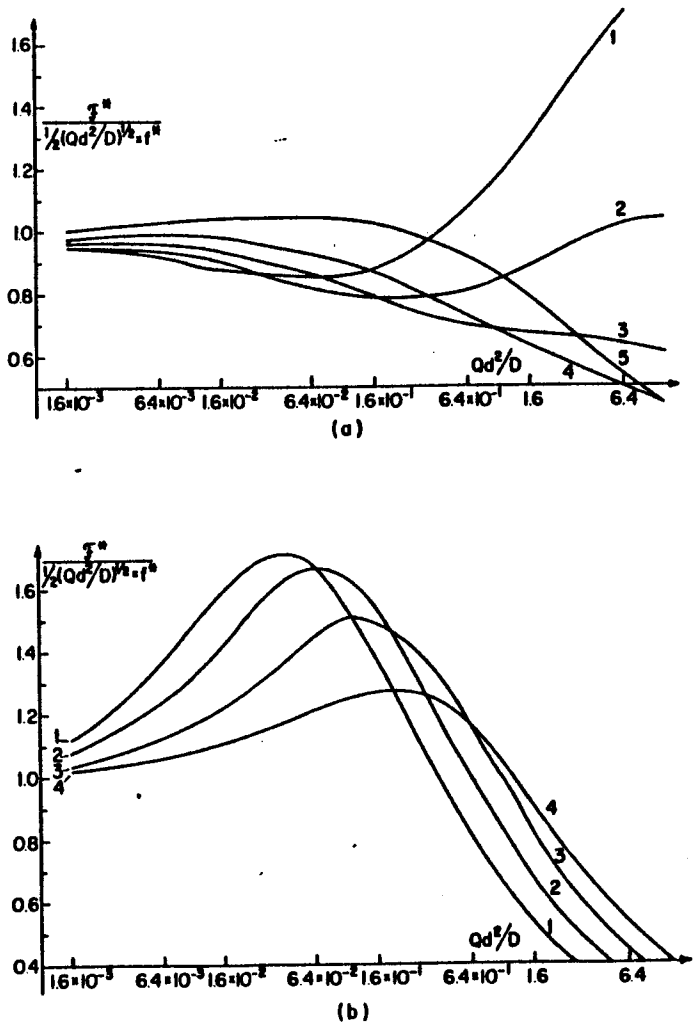


FIG. 1. (a) $\mathcal{F}^*$ divided by $\frac{1}{2}(Qd^2/D)^{1/2}f^*$ as a function of Qd^2/D (logarithmic scale). Diffusion model includes the effect of a repulsive ionic interaction with Debye-Hückel potential. The values of κd are 1/4 for curve 1, 1/2 for curve 2, 1 for curve 3, and 2 for curve 4. Curve 5 is calculated for normal diffusion without any ionic interaction. Values of f^* are 0.0901, 0.167, 0.339, and 0.603 for curves 1 to 4, respectively. Other parameters used in the calculation of $\mathcal{F}^*$ are $d = 4$ Å, $\Delta r = 0.25$ Å, $M = 200$, $f = 100$, $N = 400$, $r_N = 5054$ Å, $J^0 = 10^9$ sec^{-1}, and $|U(d)| = 5k_BT/(1+\kappa d)$. (b) Same as (a), but for an attractive ionic interaction. Also the values of f^* are 2.81, 2.17, 1.66, and 1.32 for curves 1 to 4, respectively. [By permission from Pedersen and Freed.[8]]

reaction occurs at separation d and (b) this is the distance of closest approach and (2) it automatically includes *all* reencounters. The deviation of $\mathcal{F}^*$ from this simple expression for larger Qd^2/D is shown in Fig. 1 for $J_0 d/\lambda D \ll 1$.

The correction to $\mathcal{F}^*$ for $J_0 d/\lambda D \sim 0.1 J_0 dr_{ex}/D \geq 1$ is summarized in Table I (on p. 19). It is seen that the effect of $J_0 d/\lambda D \geq 1$ is to reduce the value of $\mathcal{F}^*$. The results may be roughly expressed by

$$\mathcal{F}^*_{J=0}/\mathcal{F} = 1 + \delta'(\lambda d)^{-1} \ln[1+(J_0 d^2/D)(\lambda d)^{-1}] \ln[1+(Qd^2/D)^{\varepsilon''}] \tag{3.13'}$$

with $\delta' \sim 5/3$ and $\varepsilon'' \sim 0.45$. These results may be understood qualitatively in terms of an "exchange volume," i.e., a region extending beyond the contact distance d wherein $J(r) > Q$, so that the possibility of Q-mixing is suppressed. As we have already noted, for small Qd^2/D, the effects of reencounters after longer separations play a greater role; hence this excluded volume has less of an effect for small Qd^2/D than for larger values of Qd^2/D. This excluded volume or exchange volume effect will be seen (Section IV) to have similar functional dependences upon J_0 and Λ to the results for the effects of a finite range of $J(r)$ upon spin depolarization by Heisenberg spin exchange. The important difference with this latter effect is the nearly negligible Q-dependence in that case.

B. CIDEP: Polarizations in the Absence of Chemical Reactions

Typical results on polarizations for $\mathcal{K} = 0$ are shown in Fig. 2. These are

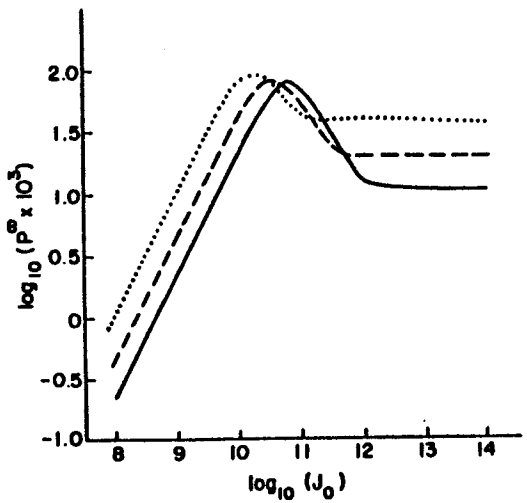


FIG. 2. P_e^∞ as a function of J_0 for initial singlet state. Solid curve: $r_{ex} = 2$ Å; dashed curve: $r_{ex} = 4$ Å; dotted curve: $r_{ex} = 8$ Å. Calculated for $D = 10^{-5}$ cm²/sec, $Q = 2 \times 10^8$ sec^{-1}, $d = 4$ Å. This graph may be scaled by converting to proper dimensionless variables. [By permission from Pedersen and Freed.[6]]

results for $J(r)$ given by Eq. (2.41). One finds that for small J_0 values these results may be approximated by

$$P_s^{\infty} \approx (Qd^2/D)^{\varepsilon} 2J_0\tau_1(\lambda) \qquad \text{for} \quad 2J_0\tau_1 \ll 1 \tag{3.14}$$

where

$$\tau_1(\lambda) \approx (d/D\lambda)[1+(\lambda d)^{-1}] \tag{3.15}$$

and $\varepsilon \sim \frac{1}{2}$ for $(Qd^2/D) \leqslant 0.016$, but $\varepsilon \to 0$ as Qd^2/D becomes larger. By comparing Eq. (3.15) with Eq. (3.7) we can regard $\tau_1(\lambda)$ as the effective lifetime of the "exchanging" radical pair. Equation (3.14) shows that for small $J_0\tau_1$, P_s^{∞} increases linearly with J_0. One sees, however, in Fig. 2 that a maximum in P_s^{∞} is achieved [the corresponding value of J_0 is referred to as $J_0(\max)$]. Then the polarization P_s^{∞} first decreases with J_0, but then levels off to a value virtually independent of J_0, i.e., $P_s^{\infty}(\text{asymp})$. One finds that this asymptotic value is dependent on r_{ex}: the larger the value of r_{ex}, the greater is $P_s^{\infty}(\text{asymp})$. This important feature has the consequence of permitting significant polarizations to develop even while J_0 may be very large. We have found that this asymptotic region is reasonably well approximated by

$$P_s^{\infty}(\text{asymp}) \approx (Qd^2/D)^{\varepsilon}\tfrac{1}{2}/(\lambda d)^{\varepsilon'} \qquad \text{for} \quad 2J_0\tau_1(\lambda) \gg 1 \tag{3.16}$$

where $\varepsilon' \sim 1$ for $\lambda d \gg 1$ and $(Qd^2/D) < 0.016$ but becomes smaller as these inequalities are violated. Accurate values of $P_s^{\infty}(\text{asymp})$ appear in Fig. 3a, while typical results for low J_0 illustrating deviations from Eq. (3.14) are shown in Fig. 3b. Equations (3.14)–(3.16) can be incorporated into the form:

$$P_s^{\infty} \approx \left(\frac{Qd^2}{D}\right)^{\varepsilon} \frac{2J_0\tau_1(\lambda)+[3/2(\lambda d)^{\varepsilon'}][2J_0\tau_1(\lambda)]^2}{1+[2J_0\tau_1(\lambda)]^2} \tag{3.17}$$

which approximates the overall behavior, but is not exact. One notes from Eq. (3.17) that

$$J_0(\max) \approx [2\tau_1(\lambda)]^{-1} \tag{3.17'}$$

A special case of the exponential decay model, referred to as the contact exchange model for which $J(r_j) = J_0\delta_{j,0}$, may be obtained by letting $\lambda d \to \infty$ in Eq. (3.17), while $\lambda^{-1} \to \Delta r_j$ in Eq. (3.15) for τ_1. This yields

$$P_s^{\infty} \approx (Qd^2/D)^{\varepsilon} 2J_0\tau_1/[1+(2J_0\tau_1)^2] \tag{3.18}$$

with

$$\tau_1 = d\Delta r_j/D \tag{3.19}$$

where Eq. (3.19) is very similar to Eq. (3.7) except Δr_j is the very small extent of the exchange region. Note that this limiting model has lost the important feature of having any asymptotic polarizations $P_s^{\infty}(\text{asymp})$ for large J_0.

One notes that ε of Eq. (3.17) decreases from the simple value of $\frac{1}{2}$ for values of Qd^2/D that are an order of magnitude smaller than those for which the appropriate CIDNP expression, Eq. (3.13), shows similar departures.

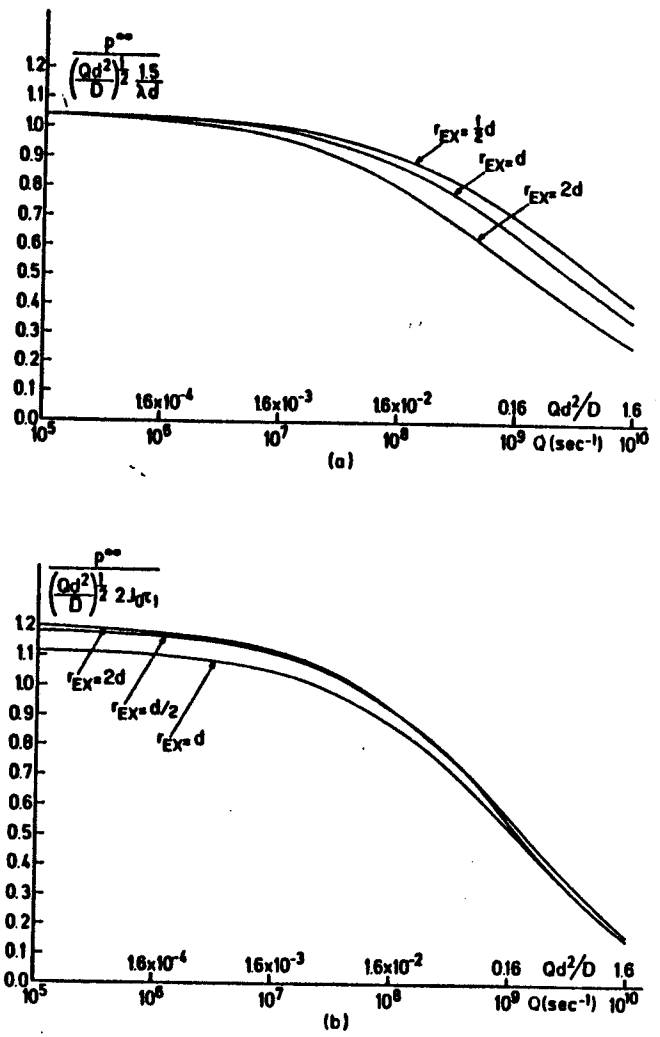


FIG. 3. (a) $P_s^{\infty}(\text{asymp})$ divided by $\frac{1}{2}(\lambda d)^{-1}(Qd^2/D)^{1/2}$ as a function of Qd^2/D. The asymptotic polarizations are for $2J_0\tau_1 \gg 1$. The different curves are for $r_{ex}/d = 1/2$, 1, and 2. The abscissa is also labeled as Q for which $D = 10^{-5}$ cm²/sec and $d = 4$ Å should be used. The signs of the polarization are determined as follows. (i) No chemical reaction: $\text{Sign}[P_s^{\infty}] = -[\text{Sign}\,Q][\text{Sign}\,J]\{\text{Sign}[\rho_{SS}(t=0)-\rho_{TT}(t=0)]\}$; (ii) spin-selective chemical reaction (reaction of S states): $\text{Sign}[P_s^{\infty}] = [\text{Sign}\,Q][\text{Sign}\,J]$. (b) P_s^{∞} divided by $2J_0\tau_1(Qd^2/D)^{1/2}$ as a function of Qd^2/D. These are the values appropriate for $2J_0\tau_1 \ll 1$. The different curves are labeled as in (a) and the signs of the polarization are determined as in (a). Also τ_1 is defined by Eq. (3.15).

That is, the reencounter mechanism is more likely to be less important [in the limits of Eq. (2.16)] for CIDEP than CIDNP. This follows from the Q-mixing pathways given by Eqs. (2.36a,b) and Eq. (2.38), which show that CIDNP requires two distinct Q-mixing steps, while CIDEP requires only one. Thus, for CIDEP, as Qd^2/D becomes very small, the required S-T_0 mixing becomes optimal more quickly for all Q values, so that the polarization becomes almost independent of Q.

The fact that $P_a^\infty \to P_a^\infty(\text{asymp})$ for $J_0\tau_1(\lambda) \gg 1$ may be rationalized in terms of the fact that the effective region of polarization [which includes the "desirable" range in $J(r)$, i.e., $J(r) \sim J_0(\max)$] merely moves out further from r_0, while the inner region [where $J(r) > J_0(\max)$] is primarily effective in quenching any polarization by a Heisenberg spin exchange mechanism (see below).

One may at this stage question the sensitivity of these asymptotic results to the specific functional dependence of $J(r)$ upon r. Thus different alternate forms were considered, in particular modified exponentials: $J(r) = (d/r)^n J_0 e^{-\lambda(r-d)}$ ($n = -1$, 0, or 1) and also $J(r) = (d/r)^n$ ($n = 6$ or 12). Very similar results are obtained for all three exponential forms including the magnitude of $P_a^\infty(\text{asymp})$ for large J_0. The r^{-6} form for $J(r)$ behaves somewhat differently yielding generally higher values for P_a^∞ and it continues to increase as J_0 gets larger. The results for r^{-12} are more similar to those for the exponential forms, showing some leveling effects as J_0 gets larger. In general, however, one expects exponential forms for (medium range) exchange forces.

C. CIDEP: Polarizations in the Presence of Chemical Reactions

When one introduces the $\mathscr{K}$ of Eq. (2.40), then one is able to relate the polarizations generated in the presence of a spin-selective chemical reaction to those in its absence by a series of exact relations analogous to Eqs. (3.3)–(3.5) for CIDNP. First, the analog of Eq. (3.5) is

$$P_a^\infty(\text{R.I.})/\mathscr{F}(\text{R.I.}) = -P_{a,k=0}^\infty(S) = P_{a,k=0}^\infty(T_0) \tag{3.20}$$

where the subscript $k = 0$ indicates no chemical reaction. The quantity $\mathscr{F}(\text{R.I.})$ is often approximated as $\mathscr{F}_0(\text{R.I.}) = \frac{1}{2}\Lambda$ and the small corrections may be obtained from Eqs. (3.3)–(3.5) and the discussions on $\mathscr{F}$. By application of Eq. (3.3) and the superposition principle, Eq. (3.20) can be rearranged to give

$$P_a^\infty(S) + P_a^\infty(T_0) = \Lambda[1 + \mathscr{F}(T_0)]P_{a,k=0}^\infty(T_0). \tag{3.21}$$

Another exact relation one obtains is

$$P_a^\infty(T_0) = [1 + (1-\Lambda)\mathscr{F}^*]^{-1} P_a^\infty(T_0, \Lambda = 1) \tag{3.22a}$$

which is easily rearranged to

$$P_a^\infty(T_0) = (1 + \mathscr{F}^*)[1 + (1-\Lambda)\mathscr{F}^*]^{-1} P_{a,k=0}^\infty(T_0). \tag{3.22b}$$

Equation (3.22a) may be interpreted in a manner analogous to Eq. (3.9a). It then follows from Eqs. (2.16), (2.17), and (3.9a) that

$$P_a^\infty(S) = (\Lambda - 1)P_a^\infty(T_0) \tag{3.23}$$

which is the analog of CIDNP, Eq. (3.3).

These relations, Eqs. (3.20)–(3.23), show that even when the spin-selective chemical reaction is present, the basic CIDEP polarizing mechanism is unaltered and the P_a^∞ results for $k = 0$ may be utilized [with some small corrections involving Λ and $\mathscr{F}^*$ in Eq. (3.22b)]. In particular, Eq. (3.20) may be interpreted as follows. The chemical reaction merely acts to eliminate a fraction $\mathscr{F}$ of singlets. One may then calculate the polarization as though there were no chemical reaction, but with the initial condition $[\rho_{T_0T_0}(0) - \rho_{SS}(0)] = \mathscr{F}$. Since P_a^∞ is proportional to $[\rho_{T_0T_0}(0) - \rho_{SS}(0)]$, we see that $P_a^\infty/\mathscr{F}$ becomes independent of k and equal to $P_{a,k=0}^\infty(T_0)$.

These results are appropriate when the form of Eq. (2.40) is used for $\mathscr{K}(r)$. If the form of Eq. (2.39) were used, then there would necessarily be some changes. The effect of the off-diagonal matrix elements in Eq. (2.39) is to destroy polarization (with rate $k/2$) in the region d to $d + \Delta r_k$. If $J_0 > J_0(\max)$, then the polarization in this region is effectively quenched anyway by spin exchange, so the results are unaffected. For $J_0 < J_0(\max)$, these matrix elements do become important and one finds that $P_a^\infty(\text{R.I.})/\mathscr{F}(\text{R.I.})$ depends on k. In particular, the maximum in $P_a^\infty/\mathscr{F}$ vs J_0 as shown in Fig. 2 has virtually disappeared compared to $P_a^\infty(\text{asymp})/\mathscr{F}$,[6] which is unchanged as noted.

D. Convergence Features of the Solutions

The convergence of the finite-difference method employed here requires that (1) Δr, the finite-difference interval, be small enough; (2) r_N and r_M, the locations respectively of the outer absorbing wall and the position where $J(r)$ is negligible, be large enough; and (3) the variable s be small enough that the limit $s \to 0$ has been achieved.

We have found[6] that satisfactorily convergent solutions are obtained when Δr is chosen so that

$$J(r_l)/J(r_l + \Delta r) = e^{\lambda \Delta r} \lesssim 5 \tag{3.24}$$

and then M is taken so that

$$J(r_M) \ll Q. \tag{3.25}$$

The convergences in r_N/d and in $\sigma = sd^2/D$ are somewhat interrelated and of considerable importance in both understanding and applying the results of Section III. We first consider the convergence in σ (or s). The convergence with s is closely related to the convergence with t, and one may use the approximate relation $s \sim t^{-1}$ (or $\sigma \sim \tau^{-1}$) in relating to a time scale. In general, we find that the s needed for convergence (s_{conv}) follows

$$\sigma_{conv} \propto Qd^2/D \qquad \text{or} \qquad s_{conv} \propto Q \tag{3.26}$$

(provided r_N is sufficiently large), although for CIDNP it appears that $s_{conv} \propto Q^{0.8}$. The actual approach to the $s \to 0$ limiting values is asymptotic, so that for convenience in the discussion of this subsection, we have taken s_{conv} to be the value for which P^∞ or $\mathcal{F}$ is within 10% of its limiting value. In particular, for CIDEP one has convergence approximately for

$$s \lesssim \tfrac{1}{3}Q \tag{3.27a}$$

while for CIDNP approximately for

$$s \lesssim (1/80)Q. \tag{3.27b}$$

This large difference between CIDEP and CIDNP convergence may be understood in terms of the basic reencounter mechanism and the schemes of Eqs. (2.36) for CIDEP and Eq. (2.38) for CIDNP. It was noted that there are two Q-mixing steps for CIDNP, and only one for CIDEP. Thus reencounters after longer periods of separation (hence smaller values of s) are needed for CIDNP, i.e., the asymptotic $\mathcal{F}^*$ needed for CIDNP are developed after much longer times than the asymptotic P^∞.

This convergence with s (or t) is clearly important in the context of our approach, in which we have separated the RPM polarization-producing process as being fast compared to other processes, e.g., individual radical T_1's and radical scavenging. In particular if we recognize that typical free radical T_1's are of the order of magnitude of 10^{-6} sec, then for a reasonable $Q \sim 10^8$ sec^{-1}, one has that P^∞ is generated in about 3×10^{-8} sec, while $\mathcal{F}^*$ takes about 0.8×10^{-6} sec to develop. It is clear, then, that P^∞ may be taken as a fast process, although some doubt exists as to whether the development of $\mathcal{F}^*$ is not influenced by individual radical T_1 processes; i.e., in the latter case the two-time scale approach is beginning to break down. One can, of course, include the T_1's, etc., into the SLE and solve the resulting equations as before, since the method is quite general (see below), but this naturally complicates the physical model and the solution.

In this context of the discussion of the s_{conv} needed for Eqs. (2.16) and (2.17), one may offer a simple physical interpretation of these expressions for $s \neq 0$. It will be seen in Section VI that by letting $s \to k$, one may interpret Eqs. (2.16) and (2.17) as referring to the P^∞ and $\mathcal{F}^*$ values obtained for those

"radical pairs" that are scavenged by a (pseudo)-first-order rate process with rate constant k. That is, one solves for the $\lim_{s \to k} s\rho(s)$. Thus as $k \to 0$ Eqs. (2.16) and (2.17) refer to the $t \to \infty$ limiting values, as they should. However, when $k \gtrsim s_{conv}$, the polarization generating mechanism will be interfered with by the rate process (which can also be a T_1 process).

This consideration can have important consequences. Thus, for $k \to s > 3Q$, one finds that instead of the typical dependences of P^∞ and $\mathcal{F}^*$ on $(Qd^2/D)^\varepsilon$ with $\varepsilon \sim \frac{1}{2}$ one has instead that $P^\infty \propto (Qd^2/D)$ and $\mathcal{F}^* \propto (Qd^2/D)^2$. This reflects the fact that the polarization processes are quenched before the reencounter mechanism can be effective, and it is only the effect of the initial encounter (typically small) which can be observed. For values of $s < 3Q$, but larger than those of Eq. (3.26), the effects of reencounters are incompletely included.

The convergence of the solutions with r_N (for small enough s) has similar features. If we use the diffusion expression

$$D = \langle \Delta r^2 \rangle / 6t \approx (2r_N)^2/6t \tag{3.28}$$

then we have

$$r_N/d \approx (\tfrac{1}{3}t_{conv}\, D/d^2)^{1/2} \approx (3/2)^{1/2}/\sigma_{conv} \propto (D/Q)^{1/2}. \tag{3.29}$$

Thus, as Q decreases (or D increases), reencounters after longer distances of separation are needed to provide effective Q-mixing, and a larger r_N is required. It follows from Eqs. (3.27) that substantially larger values of r_N are required for CIDNP than for CIDEP, as has been noted.[8] Furthermore, we note that the effect of introducing some rate process with $k > s_{conv}$ will be to reduce the value of r_N needed for convergence. Alternatively, by reducing r_N, the reencounter process may be interfered with.[21]

Inclusion of Individual Radical T_1's

One can, when necessary, include the effect of spin-lattice relaxation of the radicals during the reencounter processes. This is most conveniently done by assuming that the individual radical T_1's may be introduced as though the combined density matrix of the pair of radicals is simply the direct product of the two single radical density matrices (this is a reasonable approximation for a reencounter mechanism when the time the radicals are well separated is much longer than when they are close and interacting). For the single radical density matrix elements, one has the following rate equations:

$$(d/dt)\rho_{a\mp,a\pm} = -T_{2a}^{-1}\rho_{a\mp,a\pm} \tag{3.30a}$$

$$(d/dt)(\rho_{a+} - \rho_{a-}) = -T_{1a}^{-1}(\rho_{a+} - \rho_{a-} - P_a^{eq}) \tag{3.30b}$$

[21] Note that the dependence of s_{conv} on D reported in I, actually resulted in part from using r_N small enough to interfere with the reencounter process.

with similar expressions for radical B. Here P_a^{eq} is the equilibrium value of $\rho_{a+}-\rho_{a-}$. By use of the transformation relations given after Eq. (2.15) between doublet and triplet representations, one can obtain the rate equation for the density matrix in the triplet representation. This rate equation will in general show couplings between the different matrix elements of ρ, but if one assumes for simplicity that $T_{1a}=T_{1b}=T_{2a}=T_{2b}=T_1$ and $P_a^{eq}=P_b^{eq}$, then the equations become uncoupled and one gets

$$\dot{\rho}_{ST_0} = -2T_1^{-1}\rho_{ST_0}, \tag{3.31a}$$

$$\dot{\rho}_{SS} = -2T_1^{-1}(\rho_{SS}-\tfrac{1}{4}), \tag{3.31b}$$

$$\dot{\rho}_{T_0T_0} = -2T_1^{-1}(\rho_{T_0T_0}-\tfrac{1}{4}). \tag{3.31c}$$

These equations show the expected effect of the spin-lattice relaxation: i.e., ρ_{ST_0}, which is the RPM polarization, will decay to zero, while the diagonal elements will decay to $\frac{1}{4}$; i.e., T_1 randomizes the distribution of the triplet states and the singlet state, thereby reducing any CIDNP polarization. As we have already noted, the T_1 processes are more likely to affect the CIDNP process.

When one includes Eqs. (3.31) in the SLE, then the Laplace-transformed equation is

$$(s+2T_1^{-1}+i\mathscr{H}^\times(\lambda)+\Gamma_r)\rho(s,r) = \rho(0,r)+(1/2s)T_1^{-1}(|S\rangle\langle S|+|T_0\rangle\langle T_0|) \tag{3.32}$$

in the absence of a chemical reaction. [In the presence of a chemical reaction the last term on the right-hand side of Eq. (3.32) must be modified; cf. Section VI.] In general, one must Laplace-invert Eq. (3.32) to obtain the explicit time evolution, since as $t\to\infty$, all polarizations disappear. However, for the case of CIDNP from recombination products, for example, one may use the device of obtaining $\mathscr{F}^*$ by collecting the reacting singlet particles in an inner "box" at $r<d$ with rate k as they are lost from $r_0=d$. For the diamagnetic products only, the electron spin T_1 and Q are set equal to zero. Then the limiting forms like Eqs. (2.16) and (2,17) [i.e., $\lim_{s\to 0} s\rho(s)$] are applicable. [Note that one is not taking the limit $s\to k$ that was discussed above, although the interference of the T_1 process with the polarization process will be very similar, i.e., the dependence of $\mathscr{F}^*$ on $(Qd^2/D)^\varepsilon$ may be characterized by $\varepsilon>\frac{1}{2}$.] A scavenging reaction that depletes the radicals before the end of the polarization process may be introduced with a simple change of s to $s+k$ in Eq. (3.32). Again comments similar to those for T_1 decays apply here.

In general, we note that the two-time scale approach should be a useful one, and that, when necessary, various approximate schemes of decoupling the T_1 and scavenging effects may be employed.

IV. Models Including Radical-Pair Interactions in the Diffusive Dynamics

A. Interaction Potentials

We will use the SLE equation (2.1) as we did in Section II. However, as distinct from Section II, we want the diffusion operator $D\Gamma_r$ to include effects of attraction (or repulsion) between the radicals A and B.[7] This is formally equivalent to the well-known problem of the movement of a Brownian particle in a potential field, and the (Smoluchowski) diffusion operator for the classical probability distribution p is given by

$$D\Gamma_r\, p(\mathbf{r}) = D\nabla\cdot[\nabla p+(1/kT)\,p\nabla U(r)] \tag{4.1}$$

where $D=D_a+D_b$ is again the diffusion coefficient for the relative motion between radicals A and B and $U(r)$ is the potential energy between them, assumed to depend only on r. Furthermore, we shall allow $U(r)$ to be spin-dependent; hence $D\Gamma_r$ now becomes a spin- as well as r-dependent operator.

We now define a function $F(r)$ by

$$F(r)\mathbf{e}_r = (1/kT)\nabla U(r) = (1/kT)[\partial U(r)/\partial r]\mathbf{e}_r \tag{4.2}$$

where $F(r)$ is, however, an operator in spin-space and $\mathbf{e}_r$ is the unit vector in the radial direction. Then we take advantage of the orientation independence of $\mathscr{H}_0(r)$ and $F(r)$ to obtain the following equation for $\hat{\rho}(r,t)=r\rho(r,t)$:

$$\partial\hat{\rho}(r,t)/\partial t = -i\mathscr{H}^\times(r)\hat{\rho}(r,t)+D\hat{\Gamma}_r\hat{\rho}(r,t)+\mathscr{K}_r\hat{\rho}(r,t) \tag{4.3}$$

where

$$\hat{\Gamma}_r\hat{\rho}(r,t) = [\partial^2\hat{\rho}(r,t)/\partial r^2]+(1/r)(\partial/\partial r)[\hat{F}(r)\hat{\rho}(r,t)] \tag{4.4}$$

with $\hat{F}(r)\equiv rF(r)$ and we have used the fact that $[\nabla\cdot\mathbf{e}_r F(r)] = r^{-2}(\partial/\partial r)r^2F(r)$. In general, our use of $\mathscr{K}_r$ will also differ from that of Section III.

We again seek to obtain a complete solution in the form of Eq. (2.31), where W is the transition matrix obtained by applying the finite difference technique to the diffusion operator $\hat{\Gamma}_r$. The Ω matrix is identical to that used in Section II, but the W matrix is different due to (1) the inclusion of potential forces and (2) the possible spin-dependence of $\hat{\Gamma}_r$. We first illustrate the effects of the spin-dependence of $\hat{\Gamma}_r$ by writing $i\mathscr{H}^\times-D\hat{\Gamma}_r$ in the four-dimensional spin-space for states S and T_0 in which $\hat{\Gamma}_r$ is naturally defined. That is,

$$i\mathscr{H}^\times - D\hat{\Gamma}_r = \begin{array}{c} \begin{matrix} SS & ST_0 & T_0S & T_0T_0 \end{matrix} \\ \begin{pmatrix} -D\hat{\Gamma}_{r,SS} & -iQ & iQ & 0 \\ -iQ & i2J(r)-D\hat{\Gamma}_{r,ST} & 0 & iQ \\ iQ & 0 & -2iJ(r)-D\hat{\Gamma}_{r,TS} & -iQ \\ 0 & iQ & -iQ & -D\hat{\Gamma}_{r,TT} \end{pmatrix} \end{array}. \tag{4.5}$$

Here $\hat{\Gamma}_{r,SS}$ and $\hat{\Gamma}_{r,TT}$ are, respectively, the diffusion operators for singlet and triplet states. By a simple generalization of our discussion of the inclusion of spin-selective chemical reactions, we note that for the off-diagonal elements, e.g. ρ_{ST_0}, the proper diffusion operators should be

$$\hat{\Gamma}_{r,ST} = \hat{\Gamma}_{r,TS} = \tfrac{1}{2}(\hat{\Gamma}_{r,SS}+\hat{\Gamma}_{r,TT}). \tag{4.6}$$

That is, physically, regarding $\hat{\Gamma}_r$ from a finite-difference point of view, it gives the jump rate between different values of r. As such, $\hat{\Gamma}_{r,SS}$ and $\hat{\Gamma}_{r,TT}$ yield the lifetime-uncertainty-broadening of the S and T_0 states at a specific position r due to jumps to other positions. Then Eq. (4.6) follows from the usual uncertainty-in-lifetime effects for off-diagonal density-matrix elements. A more fundamental justification of this matter is given elsewhere.[21a]

The resulting $\mathbf{W}^\alpha$ matrix appropriate for each $(N+1)$-dimensional subspace corresponding to $\alpha = SS$, ST_0, T_0S, or T_0T_0 is given by the following series of equations:

$$D^{-1}W^\alpha_{0,0} = -(2/\Delta r^2)(1+\Delta r/d) + r_1 F_\alpha(1)/\Delta r d, \tag{4.7a}$$

$$D^{-1}W^\alpha_{0,1} = 2/\Delta r^2 + F_\alpha(0)/\Delta r, \tag{4.7b}$$

$$D^{-1}W^\alpha_{j,j-1} = \Delta r^{-2} - F_\alpha(j)/2\Delta r, \tag{4.8a}$$

$$D^{-1}W^\alpha_{j,j} = -2/\Delta r^2 + (2\Delta r)^{-1}[F_\alpha(j+1)r_{j+1}/r_j - F_\alpha(j-1)r_{j-1}/r_j], \tag{4.8b}$$

$$D^{-1}W^\alpha_{j,j+1} = \Delta r^{-2} + F_\alpha(j)/2\Delta r, \tag{4.8c}$$

where $0 < j < M$ and

$$D^{-1}W^\alpha_{M,M-1} = 2/(1+f)\Delta r^2 - F_\alpha(M)/\Delta r(1+f), \tag{4.9a}$$

$$D^{-1}W^\alpha_{M,M} = -2/f\Delta r^2 - F_\alpha(M-1)r_{M-1}/r_M \Delta r(1+f), \tag{4.9b}$$

$$D^{-1}W^\alpha_{M,M+1} = 2/f(1+f)\Delta r^2, \tag{4.9c}$$

while for $M < j < N$:

$$D^{-1}W^\alpha_{j,j-1} = 1/f^2\Delta r^2 \tag{4.10a}$$

$$D^{-1}W^\alpha_{j,j} = -2/f^2\Delta r^2 \tag{4.10b}$$

$$D^{-1}W^\alpha_{j,j+1} = 1/f^2\Delta r^2 \tag{4.10c}$$

and

$$D^{-1}W^\alpha_{N-1,N} = 0 \tag{4.11a}$$

$$D^{-1}W^\alpha_{N,N-1} = 2/f^2\Delta r^2 \tag{4.11b}$$

$$D^{-1}W^\alpha_{N,N} = 0 \tag{4.11c}$$

[21a] L. P. Hwang and J. H. Freed, *J. Chem. Phys.* 63, 118 (1975).

where the notation is essentially the same as before. Also the condition of conservation of total probability:

$$\sum_{i=0}^{N} V(i) W^\alpha_{i,j} = 0 \qquad \text{for} \quad j = 0, 1, \ldots, N \tag{4.12}$$

has been used extensively to obtain Eqs. (4.7)–(4.11) where the radial weighting factors $V(i)$ are given by Eq. (2.27). Note that M is now chosen so that $J(r_M) \approx 0$ and $F_\alpha(r_M) = F_\alpha(M) \approx 0$. That is, for $r < r_M$ there is an r-dependent exchange interaction and a potential field against which the diffusion takes place, and small increments of Δr are required for a proper solution; while for $r > r_M$, the Hamiltonian $\mathcal{H}(r)$ is independent of r, and the diffusion is simple unhindered Brownian, so larger increments $f\Delta r$ with $f \sim 10$–100 may be utilized to adequately represent the motion. We have already pointed out that the present finite-difference technique corresponds to a description of the diffusion by a discrete Master equation. Thus, when there are restoring forces, one usually imposes the further condition on the size of Δr (beyond those given in Section III) that it be small enough that the off-diagonal elements of W are nonnegative, while the diagonal elements of W must be nonpositive. It then follows from Eqs. (4.7)–(4.11) that

$$\Delta r < |2/F_\alpha(j)| \tag{4.13}$$

where, in our models, $F_\alpha(0)$ is the largest of the $F_\alpha(j)$'s.

We again use a collecting wall at $r = r_N$. In principle, however, our explicit inclusion of valence forces removes the need for the boundary condition of a reflecting wall at $r = d$. But we have found it useful nevertheless. (Such a reflecting wall corresponds physically to a hard sphere potential with a distance of closest approach equal to d; cf. Section IV, C.)

B. Ionic Interactions

We first consider a case where Eqs. (4.1)–(4.4) and (4.7)–(4.13) are spin independent. That is, we consider interactions between charged radicals, yielding spin-independent Coulombic forces. This case has been studied by making use of the usual Debye formulas for charge-shielding effects due to the ionic atmosphere in the solution. That is, one has

$$U(r) = (e^2 Z_a Z_b/\varepsilon r)[e^{-\kappa(r-d)}/(1+\kappa d)] \tag{4.14}$$

where eZ_a and eZ_b are the charges on the radicals, and where κ, the reciprocal thickness of the ionic layer, obeys

$$\kappa^2 = (4\pi e^2/\varepsilon kT)\sum_i n_i Z_i^2 \tag{4.15}$$

where ε is the dielectric constant and n_i is the number density of the ith type of particle of charge Z_i. The results reported are for $\kappa d \geq \frac{1}{4}$, since the ionic

atmosphere effects reduce the range of the interactions thus offering computational convenience [i.e., $F(M) \approx 0$; cf. discussion after Eqs. (4.9)–(4.11)], and they are typical of aqueous ionic solutions on which HE studies have been made, i.e., a value of $U(d) = 5kT/(1+\kappa d)$ roughly corresponding to $d \sim 6$Å, $Z = 2$, and $\varepsilon = 80$ and $\frac{1}{4} \lesssim \kappa d \lesssim 2$ corresponding to $\sim 0.01M$ to greater than $0.25M$ in ionic ($Z = 2$) concentration were used, even though the quantitative validity of Eq. (4.14) is uncertain for such high concentrations.

When the ionic interactions are more long range, then the method of the previous section may easily be modified to allow for accurate solutions. One just includes the ionic interactions in Eqs. (4.10) and (4.11) so they extend out to r_N which is appropriately chosen for convergence. Also, when needed, the rate of new bimolecular encounters may easily be modified, as discussed below, to correct for charge effects.

Furthermore, in this and the next two sections, the reaction operator $\mathscr{K}_r$ in Eq. (4.3) will retain its simple significance as given by Eq. (2.40).

1. *CIDNP*

One may summarize the results for ionic interactions with Debye–Hückel potentials by noting first that Eqs. (3.1)–(3.5), (3.6) and (3.9) *again apply*. However, Eq. (3.7) must be modified to

$$\tau_1^{-1} = \tau_{1,u}^{-1} f^* \exp[U(d)/kT] \tag{4.16}$$

where

$$(f^*)^{-1} = d\int_d^\infty \exp[U(r)/kT](dr/r^2) \tag{4.17}$$

with $U(r)$ given by Eq. (4.14), and $\tau_{1,u}$ the value for uncharged radicals given by Eq. (3.7). This Debye-type correction is thus identical to that found in the usual analyses of chemical reaction kinetics.[19,20] In particular, one has the "rate constant" of new bimolecular collisions at $r = d$, which in our notation (see below) is

$$2k_2(d) = 4\pi dDf^* \tag{4.18}$$

where the quantity f^* again appears.

The effects upon $\mathscr{F}^*$ may be approximately represented (cf. Fig. 1) by

$$\mathscr{F}^* \simeq \mathscr{F}_u^* f^{*(1+\delta)} \tag{4.19}$$

where $\mathscr{F}_u^*$ are the results obtained for uncharged radicals [e.g., Eq. (3.13)] and $\delta \simeq \frac{1}{4}$ for attraction and $0 \leqslant \delta \leqslant \frac{1}{4}$ for repulsion with $Q = 10^8$ sec^{-1} ($D = 10^{-5}$ cm^2/sec), but more generally δ is somewhat sensitive to Q and κd; cf. Fig. 1, where values of $\delta \simeq 0.6$ may be found. These results indicate the complex way in which the long-range (shielded) Coulomb forces can affect the reencounter dynamics so as to influence the Q-mixing. Note, however, that

when the interaction is of short range (i.e., κd is large), then one would expect that the only effect on $\mathscr{F}^*$ would be to cause d to be replaced by an effective interaction distance of f^*d. For such cases, one would expect $\mathscr{F}^* \simeq f^*\mathscr{F}_u^*$. The small $\delta \neq 0$ in Eq. (4.19) then reflects the longer-range effect on the relative diffusive motion affecting the Q-mixing, which is an effect different from that involved in the usual descriptions of liquid-state reaction kinetics.

We have also found that Eq. (3.10) remains applicable [as well as Eqs. (3.11)] when, however, t_f is appropriately modified. The values of t_f are conveniently calculated, and we have found they obey the relation

$$t_f = 1 - f^*/f^*(r_1) \tag{4.20}$$

quite well, where

$$f^*(r_1)^{-1} = d\int_d^{r_1} \exp[U(r)/kT](dr/r^2) \tag{4.21a}$$

so that

$$f^* = \lim_{r_1 \to \infty} f^*(r_1). \tag{4.21b}$$

For r_1 such that $U(r_1)/kT \ll 1$, Eq. (4.20) simply yields

$$t_f = f^*d/r_1. \tag{4.20'}$$

It is interesting to note that such results are expected to follow from a simple argument based upon an analysis of k_f, the experimentally observed rate constant for the reaction including diffusion for steady state fluxes. Thus we may write [cf. Eq. (3.8)]

$$k_f = \Lambda 2k_2(d) = \Lambda t_f(r_1) 2k_2(r_1) \tag{4.22}$$

where $2k_2(r_1)$ is the rate of new bimolecular "encounters" at separation r_1. Thus

$$t_f(r_1) = k_2(d)/k_2(r_1) \tag{4.20''}$$

which is seen to yield Eq. (4.20) by using Eq. (4.18) and the equivalent expression for $k_2(r_1)$.

2. *CIDEP*

The general effects of attractive and repulsive forces on $P^\infty/\mathscr{F}$ were found to have typically opposite trends. Also the trends depend upon whether J_0 is large or small. For small J_0 values (i.e., $2J_0\tau_1 < 1$) attractive forces enhance P^∞ by factors of the order of 5–50 while repulsive forces diminish P^∞ with similar factors (cf. Fig. 4a). Thus, for small J_0 values, the effects of forces upon P^∞ are similar to the effects on $\mathscr{F}^*$, and one might try to rationalize this behavior in similar terms. We note that for $2J_0\tau_1 < 1$ we may approximate

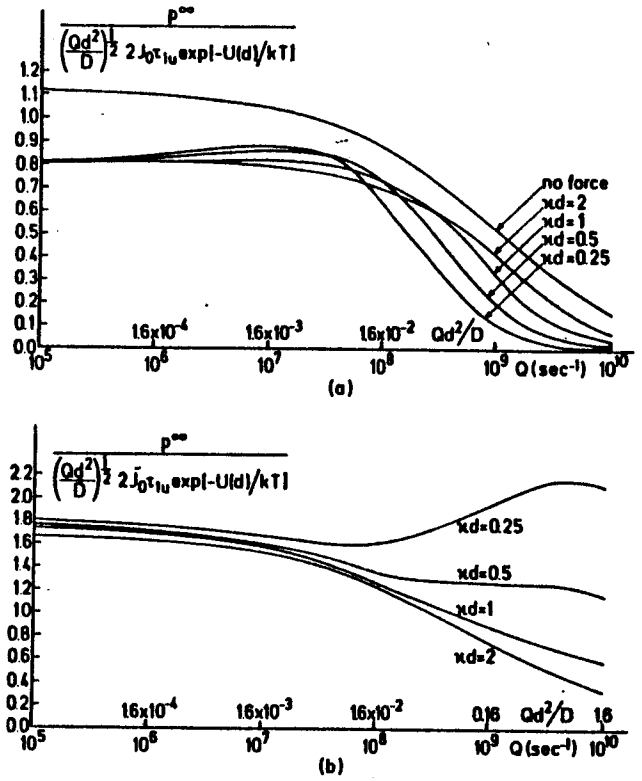
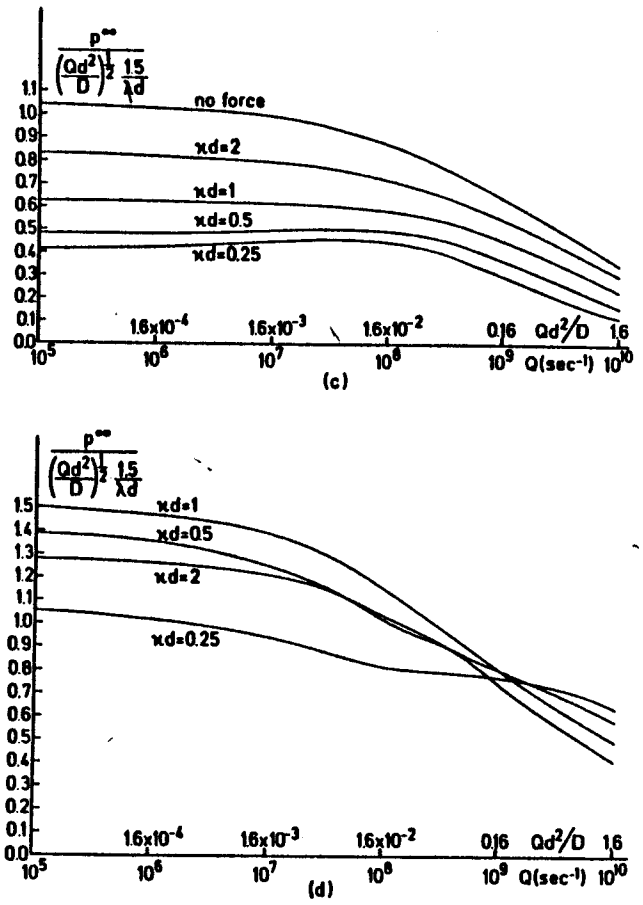


FIG. 4. (a) P_s^∞ divided by $2J_0\tau_{1u}\exp[-U(d)/kT](Qd^2/D)^{1/2}$ as a function of Qd^2/D. These values are for $2J_0\tau_1 \ll 1$, and for attractive ionic interactions. The values of κd are labeled on the graph. $r_{ss}/d = 1$, and the signs of the polarization are determined as given in Fig. 3(a). Also τ_1 is defined by Eq. (3.15). (The labeling of the abscissa in units of Q requires the use of $D = 10^{-5}$ cm²/sec and $d = 4$ Å.) (b) Same as (a) but for repulsive ionic interactions, $2J_0\tau_1 \ll 1$. (c) P_s^∞ (asymp) divided by $\frac{1}{2}(\lambda d)^{-1}(Qd^2/D)^{1/2}$ as a function of (Qd^2/D). These values are for $2J_0\tau_1 \gg 1$, and for attractive ionic interactions. The values of κd are labeled on the graph. Also $r_{ss}/d = 1$, and the signs of the polarization are determined as in (a). (The labeling of the abscissa in units of Q requires the use of $D = 10^{-5}$ cm²/sec and $d = 4$ Å.) (d) Same as (c) but for repulsive ionic interactions.

the polarization P^∞ as proportional to $2J_0\tau_1(Qd^2/D)^{1/2}$ where, as already mentioned, the $Q^{1/2}$ dependence is not very accurate, and to first order the effect of a force should be to let τ_1 have the $f^{*-1}\exp[-U(d)/kT]$ dependence and replace the distance of closest approach d by the effective contact distance f^*d in the Q-term. As a result of this simple analysis one predicts that the effect of the force upon P^∞ is given by the simple relation

$$P^\infty/P_s^\infty \cong \exp[-U(d)/kT], \tag{4.23}$$



i.e., the effect depends only upon the potential energy at the distance of closest approach and not on the explicit r-dependence of the potential. The observed trends are in accord with this simple analysis, but the relation Eq. (4.23) overestimates the actual effect probably due to the deviation of the Q-dependence from the $\frac{1}{2}$ power. This is different from CIDNP where the effects were found to be underestimated by the corresponding relation.

For high J_0-values (cf. Fig. 4c,d) one finds that the effect of the Coulomb force is much smaller and that repulsive forces generally give an enhancement (less than 50%) of P^∞ while attractive forces give a reduction by factors up to 3.

One can get a physical understanding of the Coulomb force effect on the polarization by noting that for small J_0-values the polarization is generated in the region $r \simeq d$ and this is the region to which the radicals are attracted (or repulsed). For higher J_0-values the region of effective polarization moves

out to $r > d$ (while the region $r = d$ is very effective for spin depolarization), thus giving a much smaller effect.

A more detailed presentation of the effect of Coulomb forces upon P^{∞} is given in Figs. 4a and 4b and we conclude that this effect is rather large, and in general it cannot be neglected.

We might comment at this point on the charge repulsion and ionic strength effects in Fessenden's experiments.[22] Thus by a radiolytic production of $\dot{C}H_2CO_2^-$ from $CH_3CO_2^-$ he observes a significantly lower polarization for $0.01\,M$ concentrations than for $0.1\,M$. Also $\dot{C}H(CO_2^-)_2$ was found to have smaller polarization than $\dot{C}H_2CO_2^-$. The disappearance of radicals and the polarization production were found to be due to the spin selective disproportionation of the radicals, i.e., for both radicals we have a repulsive Coulomb force (recombination of identical charged radicals). The observed trends can now be explained if the nonspherical (cf. Section VI, E) radicals are dominated by J_0 values for which $2J_0\tau_1 < 1$ such that repulsion decreases $P^{\infty}/\mathcal{F}$ and this decrease is more pronounced for smaller κd (i.e., lower ionic strength).

C. Pair-Correlation Functions

The example of ionic interactions discussed in the previous section is a case where the mean potential between interacting particles affects the dynamics. In such cases, the driving force may be thought of as one which restores the proper Boltzmann distribution as $t \to \infty$. More generally, one may introduce the equilibrium pair-correlation function $g(r)$ for the radical pair in its solvent. In particular, one notes that it may be associated with an effective mean potential of interaction $U(r)$ by

$$\ln g(r) = -U(r)/kT \tag{4.24}$$

so that one has from Eq. (4.2)

$$F(r) = -(\partial/\partial r)[\ln g(r)]. \tag{4.25}$$

The Debye–Hückel formula of Eq. (4.14) which includes charge-shielding by the solvent is clearly only one example of this. One is able to introduce improved pair-correlation functions $g(r)$, and they may readily be included in the formalism given [i.e., Eqs. (4.1)–(4.2)] even if they are only known numerically. As we have seen from our discussion of Eq. (4.14), the CIDEP/CIDNP results will definitely be sensitive to such pair-correlation effects.

Probably the simplest $g(r)$ is for two like molecules (in a solvent of like

[22] R. W. Fessenden, *J. Chem. Phys.* **54**, 2489 (1973).

molecules) interacting with hard sphere potentials. In this case:

$$U(r) = \infty \qquad r < d$$
$$U(r) = 0 \qquad r > d \tag{4.26}$$

for all pair interactions. Then to first order in the molecular number density n one has[23]

$$g(r) = 0, \qquad r < d$$
$$g(r) = 1 + (4/3)\pi n d^3[1 - (3/4)(r/d) + (1/16)(r^3/d^3)], \qquad d < r < 2d$$
$$g(r) = 1. \qquad r > 2d \tag{4.27}$$

This pair correlation function automatically includes the reflecting wall boundary condition at $r = d$, and has the simplest liquid-like correlation-function properties. These matters have been more fully explored in a discussion of spin-relaxation by dipole–dipole interaction modulated by translational diffusion.[24]

D. Space-Dependent Diffusion Coefficients (Oseen's Tensor)

The effect of the pair-correlation function $g(r)$ on the dynamics is, as we have already noted, a result of mean interactions which lead to the appropriate static Boltzmann distribution. However, better models will include "dynamical interactions" which affect the motions but do not affect $g(r)$. A particular class of such interactions may be represented by a space-dependent diffusion coefficient $D(r)$ for the relative diffusion of the radical pair.

We illustrate this class of interactions with a hydrodynamic effect, rigorously appropriate in the Brownian motion limit. This hydrodynamic interaction between Brownian particles in a liquid results from the fact that each particle creates a systematic flow pattern which affects the flow of the other particles. It is approximately taken into account for spherical Brownian particles by using a modified diffusion operator[25,25a,26]

$$\Gamma_r = \nabla \cdot [D\mathbf{1} - 2(kT)T(\mathbf{r})] \cdot \{\nabla + (kT)^{-1}[\nabla U(\mathbf{r})]\} \tag{4.28}$$

where $\mathbf{1}$ is the unit tensor and $T(\mathbf{r})$ is Oseen's tensor given by

$$T(\mathbf{r}) = (8\pi\eta r)^{-1}[1 + \mathbf{rr}(r^{-2})] \tag{4.29}$$

[23] J. de Boer, *Rep. Progr. Phys.* **12**, 305 (1949).
[24] L. P. Hwang and J. H. Freed, *J. Chem. Phys.* **63**, 4017 (1975).
[25] J. M. Deutch and B. U. Felderhof, *J. Chem. Phys.* **59**, 1669 (1973).
[25a] J. M. Deutch, *J. Chem. Phys.* **59**, 2762 (1973).
[26] R. W. Zwanzig, *Advan. Chem. Phys.* **15**, 325 (1969).

with η the solvent viscosity, D again the diffusion coefficient for the relative motion between the two radicals, and $U(r)$ is again the interaction potential between them. If $T(\mathbf{r})$ is set equal to zero, then one has the usual Smoluchowski form of the diffusion operator Eq. (4.1). The effect of $T(\mathbf{r})$ in Eq. (4.28) is to lead to diffusion with an apparent space-dependent diffusion coefficient.

The added correction to the diffusion equation, given by Oseen's tensor, is clearly an approximation. Oseen's tensor is a good approximation when the sizes and separation of the radical pair are significantly larger than the size of the solvent molecules. However, this correction is in the same spirit as any Brownian diffusion treatment of molecular diffusion and diffusion controlled molecular reaction kinetics. Thus one may hope to obtain useful insights into general trends for a space-dependent diffusion coefficient.

On considering radicals of equal radii, which should exhibit the largest hydrodynamic effect, then Eq. (4.28) becomes for spherical symmetry:

$$\Gamma_r = r^{-2}(\partial/\partial r)(r^2)[D-(kT/2\pi\eta r)][(\partial/\partial r)+(kT)^{-1}\,\partial U(r)/\partial r]. \quad (4.30)$$

By introducing the transformation $\rho(r)\rightarrow r\rho(r)\equiv\hat{\rho}(r)$ and $\Gamma_r\rightarrow r\Gamma_r r^{-1}\equiv\hat{\Gamma}_r$ one finds that the effective diffusion operator which appears in Eq. (2.10) (where $U=0$) for Oseen's tensor is now $D(r)\,\partial^2/\partial r^2$ where $D(r)=D(1-3d/4r)$. Similar changes are obtained for the other terms in Γ_r when $U(r)\neq 0$, and this justifies our remarks that the use of Oseen's tensor corresponds to an example of an apparent space-dependent diffusion constant, which acts to retard the relative diffusion as the radicals approach. The modified W-matrix is given elsewhere.[9]

1. *CIDNP*

In the presence of Oseen's tensor the quantities Λ and $\mathscr{F}^*$ are again found to remain fundamental. Also the "exact" interrelations between $\mathscr{F}(S)$, $\mathscr{F}(T_0)$, and $\mathscr{F}$(R.I.) (where R.I. refers to a random mixture of S and T_0), given by Eqs. (3.3)–(3.5) of Section III, are still obeyed.

Furthermore we can again define Λ by Eq. (3.6). In all the cases examined, we find that τ_1 may be exactly represented by [cf. Eqs. (3.7) and (4.16)]

$$\tau_1^{-1} = (D/d\Delta r_k)\,\hat{f}^*\exp[U(d)/kT]. \quad (4.31)$$

Now, however, $\hat{f}^*$ obeys

$$(\hat{f}^*)^{-1} = d\int_d^\infty \exp[U(r)/kT][r(r-3d/4)]^{-1}\,dr \quad (4.32)$$

which replaces the quantity f^* given by Eq. (4.17) that is appropriate in the absence of Oseen's tensor. One finds that Oseen's tensor effects increase τ_1 by the order of factors of 2, the effects being more pronounced in the presence of repulsive forces and less pronounced for attractive forces.[9] This increase is

expected for a mechanism that effectively slows the diffusion as the radicals approach each other.[27]

In this context, it should be noted that Deutch and Felderhof[25] have found that the mean rate of bimolecular encounters, in the case of Oseen's tensor, is given by

$$2k_2(d) = 4\pi dD\hat{f}^* \quad (4.33)$$

where $\hat{f}^*$ replaces f^*. The fact that the same correction appears in $2k_2(d)$ and τ_1^{-1} may be understood quite simply. That is, the equilibrium constant K between (nonreacting) radical pairs and separated radicals is given by

$$K = 2k_2(d)/\tau_1^{-1} \quad (4.34)$$

and it is of course independent of the molecular dynamics. Oseen's tensor only causes the diffusion to be space-dependent. It does not change $U(r)$. Thus K must be independent of whether or not Oseen's tensor is included. The fact that $\hat{f}^*$ should appear in Eq. (4.31) is easily obtained analytically in the standard manner[19] from the steady-state flux expressions given by Deutch and Felderhof.[25]

Furthermore we have found that t_f [cf. Eqs. (3.10a) and (4.20)] is well represented by the expression

$$t_f = \hat{f}^* d/r_1 \quad (4.35)$$

where $r_1 \gg d$, by analogy with our previous result Eq. (3.19′) involving f^* instead of $\hat{f}^*$. More generally, one expects from our previous results that

$$t_f = 1-\hat{f}^*/\hat{f}^*(r_1) \quad (4.36)$$

where

$$\hat{f}^*(r_1)^{-1} = d\int_d^{r_1}\exp[U(r)/kT][dr/r(r-\tfrac{1}{4}d)] \quad (4.37)$$

such that

$$\hat{f}^* = \lim_{r_1\rightarrow\infty}\hat{f}^*(r_1). \quad (4.37a)$$

We now turn to an analysis of $\mathscr{F}^*$. Again Eqs. (3.9) which relate $\mathscr{F}(T_0)$, $\mathscr{F}(S)$, and $\mathscr{F}$(R.I.) to $\mathscr{F}^*$ and Λ are found to apply exactly. We give in Figs. 5a and 5b the corrections to $\mathscr{F}^*$ due to Oseen's tensor for attractive and

[27] Oseen's tensor may be replaced by Stokes' tensor in the analysis.[25,25a] This form is perhaps more accurate for considering short-range hydrodynamic interactions. Note, however, that Eq. (4.32) follows from Eq. (4.17) by replacing r^2 by $r^2[1-(3d/4r)]$ which is equivalent to the transformation of $D\rightarrow D(r)$ [cf. the discussion after Eq. (4.30)]. Therefore, one might expect that the use of Stokes' tensor,[6] where $D(r)=r^2[1-(3d/4r)(1-d^2/12r^2)]\,D$ for equal size spherical molecules, would result in replacing r^2 in Eq. (4.17) by $r^2[1-(3d/4r)(1-d^2/12r^2)]$. Such a replacement suggests that there would be little effect in the use of Stokes' tensor instead of Oseen's tensor.

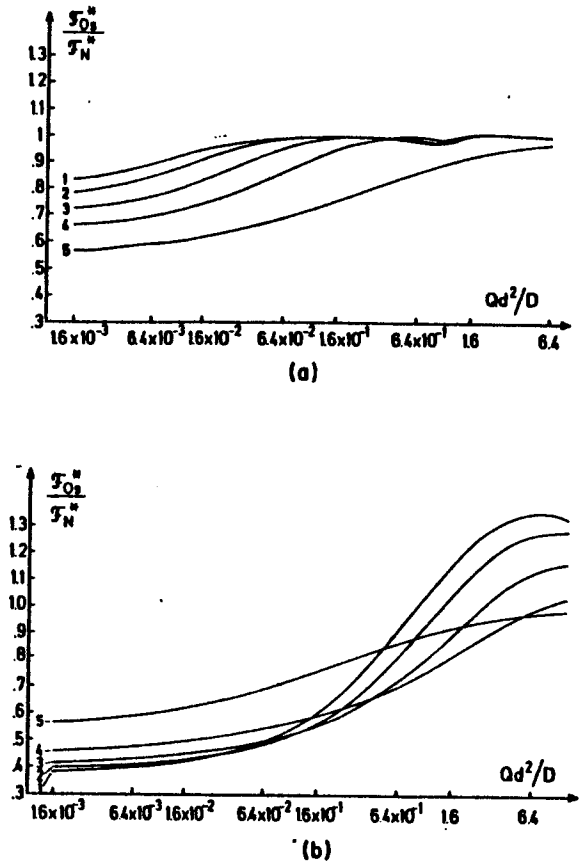


FIG. 5. (a) $\mathcal{F}^*_{Os}/\mathcal{F}^*_N$ vs Qd^2/D. Here $\mathcal{F}^*_{Os}$ is the value for $\mathcal{F}^*$ calculated with Oseen's tensor and $\mathcal{F}^*_N$ is the value neglecting Oseen's tensor. Curves 1, 2, 3, 4, and 5 are for $\kappa d =$ 1/4, 1/2, 1, 2, and no Coulomb forces, respectively (cf. Fig. 1). Results are for attractive forces. A low value of $J_0 = 10^5$ sec^{-1} has been used. [By permission from Pedersen and Freed.[9]] (b) Same as (a) but for repulsive forces. [By permission from Pedersen and Freed.[9]]

repulsive (shielded) Coulomb forces and no forces. As was the case for τ_1, repulsive forces yield greater effects than no forces and attractive forces yield smaller effects. In general, the greater effects are obtained for small values of Qd^2/D. In fact, the ratios $\mathcal{F}^*_{Os}/\mathcal{F}_N{}^*$ (cf. Fig. 5) appear to be approaching those of τ_1/τ_1(Os) as $Qd^2/D \to 0$. But for large values of Qd^2/D, the ratios $\mathcal{F}^*_{Os}/\mathcal{F}_N{}^*$ appear to approach unity, an effect most pronounced for attractive forces. The result for small values is easily interpreted by recognizing in this region that, in the absence of potentials and Oseen's tensor effects (for small J_0),

Eq. (3.13) holds for $\mathcal{F}^*$ and one should, to a first approximation, replace d by f^*d (or $\tilde{f}^*d$), i.e., this is the region where reencounters after large separations are important, so the dominant effect of the shorter-range interactions is to introduce an effective contact distance into the dynamics. For larger Qd^2/D, Eq. (3.13) is no longer appropriate, the effects of the initial encounter become more important, and one has $\mathcal{F}^* \propto (Qd^2/D)^\varepsilon$ with $\varepsilon < \frac{1}{2}$, so the dependence on $\tilde{f}^*$ decreases. One should note that Figs. 5 are calculated for a very small value of the exchange interaction $J_0 = 10^5$ sec^{-1}, which serves to exclude any effect of a finite exchange region. Some of our numerical results for more realistic values of J_0 are given in ref. 9. In general the effect of larger J_0-values (that increases with increasing J_0 and r_{ex}/d) is to decrease $\mathcal{F}^*_{Os}/\mathcal{F}_N{}^*$. For $Q = 10^8$ sec^{-1}, $d = r_{ex} = 4$ Å, and $D = 10^{-4}$ cm^2/sec, this reduction is negligible but for $D = 10^{-6}$ cm^2/sec there is a reduction of approximately 20%. These dependences may be understood by arguments similar to those already used. The trajectories in the exchange region become more important when J_0 (and r_{ex}/d) increases and D decreases (i.e., the diffusion slows down). In the exchange region the Q-mixing is suppressed and consequently $\mathcal{F}^*$ is decreased. Since the Oseen's correction to the diffusion equation corresponds to a slowing down of the diffusion when the particles are close together, one would expect $\mathcal{F}^*_{Os}$ to decrease more than $\mathcal{F}_N{}^*$ as is indeed observed from the numerical results.

2. *CIDEP*

We give in Figs. 6a and b the corrections to $P^\infty/\mathcal{F}$ due to Oseen's tensor for attractive and repulsive (shielded Coulomb forces) and no forces. The results may be rationalized in terms of trends similar to those found for CIDNP. That is, for small J_0, $[P^\infty/\mathcal{F}]_{Os}/[P^\infty/\mathcal{F}]$ shows trends predicted by the product of τ_{1Os}/τ_1 and $\mathcal{F}^*_{Os}/\mathcal{F}^*$, as expected from Eq. (3.14). For $Qd^2/D < 0.016$ we have $\varepsilon = \frac{1}{2}$ in Eq. (3.14), i.e., $\mathcal{F}^* = (Qd^2\tilde{f}^{*2}/D)^{1/2}$ and consequently $[P^\infty/\mathcal{F}]_{Os}/[P^\infty/\mathcal{F}] = 1$. For larger Qd^2/D values, $\varepsilon \to 0$ and we get $[P^\infty/\mathcal{F}]_{Os}/[P^\infty/\mathcal{F}] \to f^*/\tilde{f}^*$. These effects are such as to increase $P^\infty/\mathcal{F}$ by a factor of the order of 1.1–3. The results for high J_0 typically show only a small effect from Oseen's tensor, since the region of $r \sim d$, for which Oseen's tensor corrections are a maximum, has become relatively unimportant in the polarization process. A more quantitative discussion of the behavior for large J_0 does not seem possible at present because we only have a qualitative understanding of Eq. (3.16) even in the absence of forces. For intermediate values of J_0 the qualitative behavior is given by Eq. (3.17). One should note that J_{max} is given by $2J_{max}\tau_1(\lambda) \simeq 1$ and since τ_{1Os} and τ_1 are different, the maximum occurs for different values of J_0 and consequently $[P^\infty/\mathcal{F}]_{Os}/[P^\infty/\mathcal{F}]$ can show an oscillation for intermediate J_0 values.[9]

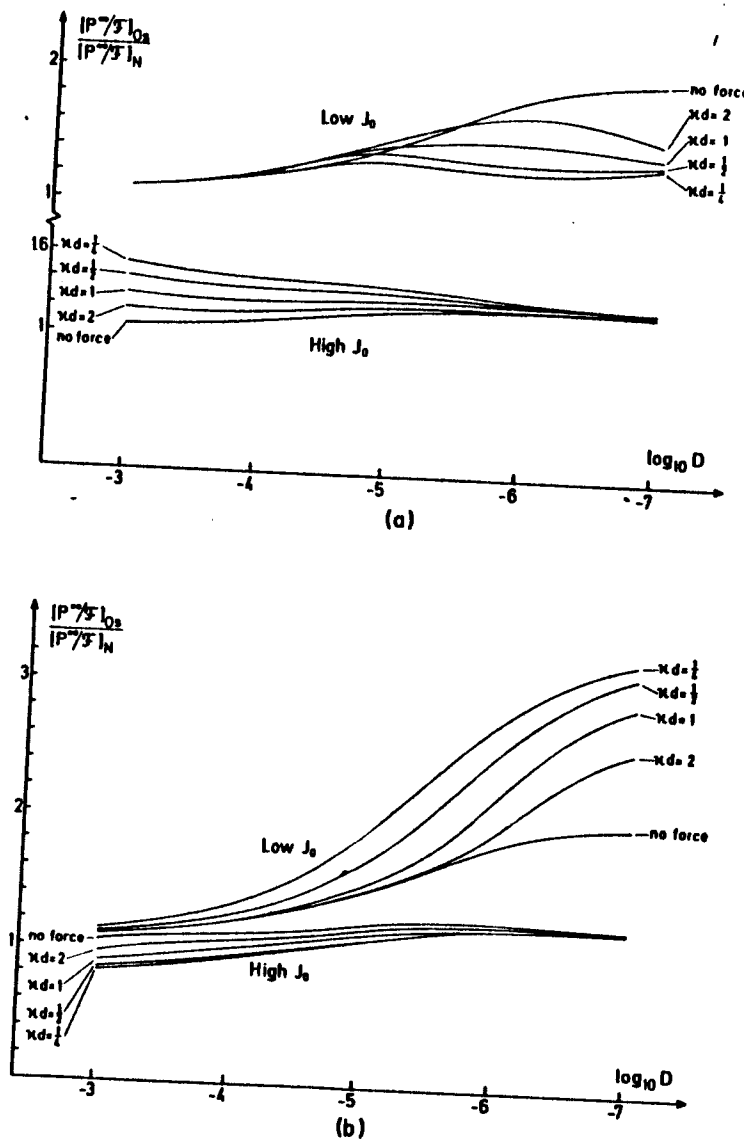


FIG. 6. (a) Graphs of $[P^{\infty}/\mathcal{F}_{Os}]/[P^{\infty}/\mathcal{F}]_N$ vs D. Here the subscripts Os and N refer to results calculated with Oseen's tensor and neglecting Oseen's tensor, respectively. Results are for attractive forces. The low J_0 results (upper curves) were calculated with $J_0 = 10^5\,\text{sec}^{-1}$, while the high J_0 results (lower curves) are for $J_0 = 10^{13}\,\text{sec}^{-1}$. Other parameters used are $Q = 10^8\,\text{sec}^{-1}$, $r_{ss} = d = 4$ Å. [By permission from Pedersen and Freed.[9]] (b) Same as (a) but for repulsive forces. [By permission from Pedersen and Freed.[9]]

E. Self-Consistent [or Exchange Forces Present (EFP)] Model

We now turn our attention to the problem of including spin-dependent diffusion in the manner indicated by Eqs. (4.5) and (4.6). In particular, we wish to include spin-dependent valence forces in the diffusive trajectories.

1. *Potential Surfaces*

We show in Fig. 7 the representation of $U_a(r)$ which has been employed to include valence interactions. This has been chosen by analogy to the well-

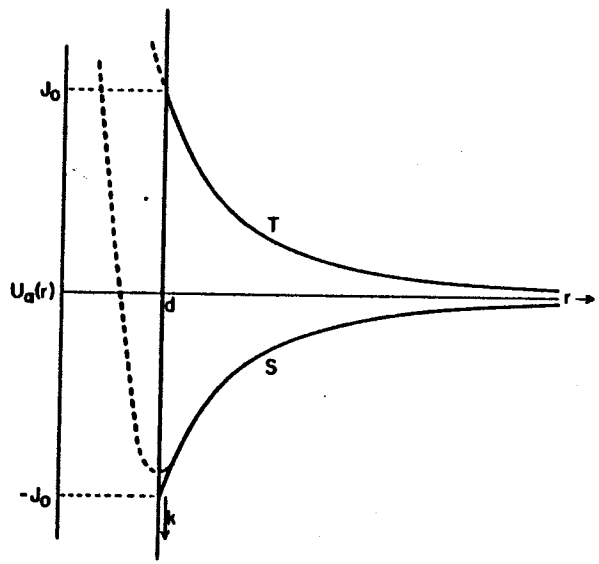


FIG. 7. Spin-dependent potentials $U_a(r)$ as a function of r, the interradical separation. The solid curves labeled S and T represent the exchange potentials utilized for singlet and triplet states, respectively, with a reflecting wall at $r = d$. The dashed lines represent the usual continuation of the potentials in the absence of a reflecting wall. [By permission from Pedersen and Freed.[7]]

studied, hydrogen-atom-pair potential surfaces as well as for computational convenience. That is, we write $U_{SS}(r) \simeq (H_0 + H_1)/(1+S)$ and $U_{TT}(r) \simeq (H_0 - H_1)/(1+S)$, where H_0 is the "Coulomb integral," H_1 the exchange integral which we shall write as $-\hbar J(r)$, and S is the overlap integral. The usual S and T energy surfaces are shown by the solid curves for $r > d$ and the dashed curves for $r < d$. We take d to be the interradical distance characteristic of the stable bond. We introduce a reflecting wall at $r = d$ [i.e., $U_{SS}(r) = U_{TT}(d) = \infty$ for $r < d$] as a convenient approximation to the repulsive terms which dominate both the S and T curves at short internuclear

distances. Then for $r > d$ we note that usually H_1 is several times larger than H_0 and is the main source of the attractive forces, while S tends to be small. Thus for convenience we let

$$U_{SS}(r) \approx -U_{TT}(r) \approx -\hbar J(r), \qquad r > d \tag{4.38}$$

and it is reasonable to approximate $J(r)$ for $r > d$ by an exponential decay in r [cf. Eq. (2.41)]. We refer to our model based upon Eqs. (4.38) and (2.41) as an exchange forces present (EFP) model as distinct from the model of Section III which we refer to as an exchange forces absent (EFA) model. It follows from Eq. (4.2) that

$$F_{SS}(r) = -F_{TT}(r) = (\lambda\hbar J_0/kT)\exp[-\lambda(r-d)] \tag{4.39a}$$

and from Eq. (4.6) that

$$F_{ST_0}(r) = F_{T_0S}(r) = \tfrac{1}{2}[F_{SS}(r)+F_{TT}(r)] = 0. \tag{4.39b}$$

That is, while the singlet terms in ρ diffuse under an attractive potential and the triplet terms under a repulsive potential, the ρ_{S,T_0} terms experience normal Brownian diffusion. [It is essentially this argument which has encouraged us to favor Eq. (2.40) rather than Eq. (2.39).] Note that in the present case, where valence forces can explicitly lead to "bonding" in which $r \approx d$ for long periods, it is often useful to consider

$$P_s^{\infty}(N) = -2\,\mathrm{Re}\lim_{s\to 0}\hat{\rho}_{ST_0}(N,s) \tag{4.40}$$

which represents just the polarization of the separated particles at $t \to \infty$ instead of P_s^{∞} given by Eq. (2.33), which includes all particles. Similarly, the probability of survival per collision $\mathscr{P}$ is given by Eq. (2.32), where (since $T_{\pm}$ states are being neglected) $\mathscr{P}(t=0) = 1$, i.e., the density matrix is normalized at time zero. However, the fraction of particles which have separated at $t \to \infty$ is

$$\mathscr{P}(N) = \lim_{s\to 0} V(N)[\hat{\rho}(N,s)_{SS}+\hat{\rho}(N,s)_{T_0T_0}]. \tag{4.41}$$

For the probability of reaction during a collision one has

$$\mathscr{F} = 1 - \mathscr{P} \quad \text{or} \quad \mathscr{F}(N) = 1 - \mathscr{P}(N). \tag{4.42}$$

In Section II, where the spin-selective chemical reaction was represented by an irreversible chemical rate ($\mathscr{K} \neq 0$) which merely "destroys" the radical, one had $P_s^{\infty} = P_s^{\infty}(N)$, $\mathscr{P} = \mathscr{P}(N)$, and $\mathscr{F} = \mathscr{F}(N)$. In the present case we can set $\mathscr{K} = 0$. Then an attractive singlet potential will trap singlet radical pairs at $r \approx d$. But they are not lost to the system, so that $\mathscr{P}(t) = 1$ for all t, and properly one should look at the $P_s^{\infty}(N)$, $\mathscr{P}(N)$, etc., for the separated radicals, which contribute to the ESR spectrum. However, we note that the diffusion Eq. (4.1) automatically includes detailed balance, so that as long as

$U(r)$ remains finite, there will still be a finite probability that a "bound" pair of radicals can separate even though $U(r = d)$ is very large. But, because the absorbing wall at $r = r_N$ is kinetically irreversible (representing, in a sense, infinite space for the relative diffusion of a single radical pair), as $t \to \infty$ even the "tightly bound" pairs must separate to r_N. This feature can be overcome by either (1) considering finite but long times and by studying $P_s(N,t)$, etc., or by (2) introducing an irreversible kinetic process which permanently removes the strongly bound radical pairs as they form by valence attractions and by studying $P_s^{\infty} = P_s^{\infty}(N)$, $\mathscr{P} = \mathscr{P}(N)$. We have used method (2) primarily because of its computational convenience, but we have made some effort[7] at a comparison of results for the two methods.

We thus define a "first-order chemical rate constant" $k(r)$ which gives the rate at which a singlet radical pair, tightly bound by the attractive valence forces between singlets [i.e., $F_{SS}(r \approx d)$], is irreversibly removed from the system, so that it can never again dissociate even as $t \to \infty$. We again use the simple form of Eq. (2.37) so that only the singlet radical pairs in the contact range d to $d+\Delta r$ are affected. This is indicated in Fig. 7. In this application, the use of k is thus largely that of a computational artifact. A large value of k guarantees that the singlet radical pair remains bound, while a small value of k does not fully prevent them from separating as $t \to \infty$. One may, in a sense, think of this k as a crude means of adjusting for momentum relaxation.

2. *Initial Conditions*

In Section II the initial condition of $\rho_0(r) = \rho_0\delta(r-r_0)/r_0^2$ (where ρ_0 is the initial r-independent spin-density matrix) was utilized throughout, since for the models considered there, either (1) Q-mixing (or polarizations) started upon initial formation of the radical pair or (2) equal amounts of S and T_0 radical pairs formed from random encounters had to reach $r_0 = d$ to react by the spin-selective chemical reaction before the polarization could begin. For the current model being considered, the actual diffusion rates, as well as relative equilibrium probability distributions, differ for the S and T_0 spins so that case (2) (R.I. initial) can only be rigorously considered by starting the radical pair initially at $\rho_0(r) = \rho_0\delta(r-r_1)/r_1^2$ where $J(r_1) \approx 0$; i.e., the inter-radical separation is large enough that their various interactions are negligible. We discuss these matters primarily from the viewpoint of CIDEP. We can use the standard Brownian motion result for the "rate constant" of new bimolecular collisions which involve either S or T_0 states only:

$$k_2(r_1) = 2\pi r_1 D. \tag{4.43}$$

There is no f^* correction since r_1 has been chosen so that $J(r_1) \approx 0$. The appropriate CIDEP intensity M_z^a contribution is (cf. Section VII):

$$dM_z^a/dt]_{k_2} = k_2(r_1)n_a(t)n_b(t)[P_s^{\infty}(r_1)-\Delta P(r_1)2\,\mathrm{Re}\,\rho_{S,T_0}(t)] \tag{4.44}$$

where the explicit dependence on initial r_1 is indicated, and $n_a(t)$ and $n_b(t)$ are the number densities of radicals A and B. $\Delta P(r_1)$ is defined as the fractional change in the polarization from that which exists at the onset of the collision, and is discussed in the next section. Now, if the effect of valence forces on the diffusive motion were neglected as in Section II, then the first term in Eq. (4.44) could equally well be written in the form

$$k_2(d)\, n_a(t)\, n_b(t)\, P_a^{\infty}(d)$$

since, as already noted above, the polarization effects do not begin until $r = d$, and the time evolution of our expressions with initial condition $r = r_1$ would just involve simple diffusion until the value $r = d$ is reached. That is, one would have

$$k_2(d)\, P_a^{\infty}(d) = k_2(r_1)\, P_a^{\infty}(r_1). \tag{4.45}$$

To get around the arbitrariness of initial condition r_1, we usually employ a *transferred* polarization $P_a^{\infty}(d_t)$ given by

$$P_a^{\infty}(d_t) \equiv [k_2(r_1)/k_2(d)]\, P_a^{\infty}(r_1)$$

$$= (r_1/d)\, P_a^{\infty}(r_1) \xrightarrow[r_N]{\text{finite}} d^{-1}(r_1^{-1} - r_N^{-1})^{-1}(1 - d/r_N)\, P_a^{\infty}(r_1) \tag{4.46}$$

where the arrow points to the expression corrected for an absorbing wall at $r = r_N$ (cf. I). Note that when the effects of valence forces on the diffusion are included, then $P_a^{\infty}(d_t)$ is no longer the true polarization developed with initial condition $r = d$, but this definition allows us to compare results of $P_a^{\infty}(d_t)$ for different initial values of r without having to correct for the differences in $k_d(r_1)$. In a similar manner we can introduce a transferred $\Delta P(d_t)$.

3. *Polarization Quenching*

As we have already noted, the quenching of initial polarization due to Heisenberg spin exchange (HE) upon a random collision is also an important process in analyzing CIDEP, if the overall kinetics of the problem is to be dealt with adequately, such as by Eq. (4.44). This polarization quenching can take place even when the bimolecular collision does not induce any spin-selective chemical reaction.

The polarization quenching is readily obtained by our methods described above. One has only to select as the initial condition $2\,\mathrm{Re}\,\rho_{S,T_0} = 1$ [cf. Eq. (4.44)] or, more precisely,

$$2\,\mathrm{Re}\,\rho_{S,T_0}(r) = \delta(r - r_1)/r_1^2 \tag{4.47}$$

(while the other initial values are $\rho_{SS} = \rho_{TT} = \mathrm{Im}\,\rho_{S,T_0} = 0$). The calculation based on Eqs. (4.3) and (2.16) then leads to

$$-\Delta P(r_1) = P_a^{\infty}(r_1, \rho_{S,T_0}(t) \neq 0) - 1 \tag{4.48}$$

where $P_a^{\infty}(r_1, \rho_{S,T_0}(t) \neq 0)$ is the polarization which remains at the end of the collision, after having started with the initial condition given by Eq. (4.47). The quantity $\Delta P(r_1)$ appears in Eq. (4.44), and the validity of Eq. (4.45) rests on recognizing that the SLE is linear and homogeneous in $\rho(r, t)$, so one may superpose solutions obtained for simple initial conditions to obtain solutions for the more complex initial conditions. We can again define a transferred $\Delta P(d_t)$ in exactly the same manner as Eq. (4.46) for $P_a^{\infty}(d_t)$. Note, however, that $\Delta P(d_t)$ is not equal to $\Delta P(d)$ for finite values of J_0 and r_{ex}, since the spin depolarization by HE will start for $r_1 > d$ as long as $|J(r_1)| > 0$. Note, also, that by Eq. (4.39b) the diffusion of ρ_{ST_0} is unaffected by the valence forces illustrated in Fig. 7, and also that the depolarization, even for random collisions, begins well before radicals approach near to d (i.e., the region where valence forces may significantly affect the motions).

4. *CIDNP Results (EFP)*

When one analyzes the results for the EFP model, one notes that the important relation, Eq. (3.6), for the "reactivity" Λ as a function of k and τ_1 again applies when τ_1 is corrected for the exchange force attraction (i.e., the singlets see an attractive potential). The τ_1 correction is identical to that used for the Coulombic potential, Eq. (4.16), but with $U(r)$ replaced by $\hbar J(r)$. When $\hbar J_0/kT \gg 1$ the radical trapping effect due to the potential becomes so large as to overwhelm any effects of k for smaller k values ($k \leqslant 10^8\ \mathrm{sec}^{-1}$). This point indicates, of course, that a more detailed description of the reaction dynamics will yield a somewhat different approach to expressing Λ than that which we have found in this work and which relates simply and directly to the familiar theories of reaction kinetics in solution. The radical trapping effect is further discussed below.

We next wish to point out that the relations for $\mathscr{F}(\Lambda) - \mathscr{F}_0(\Lambda)$ do apply provided $\Lambda > 10^{-3}$. The reason that these relations do not apply for $\Lambda < 10^{-3}$ will be discussed below, but it should be pointed out that the CIDNP effect (i.e., $\mathscr{F} - \mathscr{F}_0$) is usually too small to be experimentally observable when $\Lambda < 10^{-3}$. When these relations apply, one may concentrate on the $\mathscr{F}^*$ dependence, and it was found that Eq. (4.19) applies with $\delta = 0$ (i.e., d is replaced simply by df^*) as expected for very short-range interactions.

Also, we wish to note some points which emerge within the context of the EFP model. (1) Since substantial CIDNP polarizations require non-negligible values of Λ, which is a function of the magnitude of J_0, then values of $\hbar J_0/kT > 1$ are needed, and this implies the importance of corrections for

the finite range and magnitude of $J(r)$. (2) When $J(\mathbf{r}_i, \mathbf{r}_j)$ is not spherically symmetric, then one expects that the primary effect on the analysis is to cause a reduction in the magnitude of Λ over that for a spherically symmetric $J(r)$, i.e., only that fraction of reencounters for which $\hbar J(\mathbf{r}_i, \mathbf{r}_j)/kT > 1$ is important and their description involves a correction for the finite magnitude of J. The role played by nonspherical symmetric $J(\mathbf{r}_i, \mathbf{r}_j)$ will be seen to be different in CIDNP than for CIDEP.

5. *CIDEP Results (EFP)*

The effects of an exchange force upon the CIDNP parameters may be summarized as a very pronounced enhancement of the collision time τ_1 for $\hbar J_0/kT \lesssim 1$ but a rather small effect on $\mathcal{F}^*$ (i.e., on the diffusive motion outside the exchange region) due to the short-ranged nature of the force. We remind the reader that the presence of an exchange force is by itself identical to a spin-selective reaction, and therefore the device of including the kinetically irreversible reaction at $r = d$ [i.e., the $\mathcal{K}$-term in Eq (2.40)] could seem to be unnecessary. But, however strong the exchange force may be, there is still a finite probability that the particles bound by this potential will separate; and as $t \to \infty$ all particles will have separated.

The results given in II included the kinetically irreversible "reaction" at $r = d$ to guarantee sensible behavior in the limit $t \to \infty$. We tested the results for the EFP model without the presence of this device, by examining results for finite times. This was done simply by using the well-known Fourier (and Laplace) inversion result that the behavior at time t is dominated by values of $s \sim t^{-1}$. We have compared the time it takes for radical pairs initially at $r = d$ to collect at $r_N = 22$ Å, a separation where exchange forces are negligible. The results for EFA are, of course, independent of J_0; and for $D = 10^{-5}$ cm^2/sec 3% of the radicals have not reached r_N by $s^{-1} = 2.5 \times 10^{-8}$ sec. However, for EFP and $\hbar J_0/kT = 10$ about 7% of the radicals have not reached r_N by 2.5×10^{-7} sec, while for $\hbar J_0/kT = 25$ all but 5% have reached r_N by $s^{-1} = 2.5$ sec. The results for $\hbar J_0/kT = 25$ show a plateau where nearly all the triplets have been collected by $s^{-1} = 2.5 \times 10^{-8}$ sec, but the singlets do not begin to be collected until $s^{-1} = 2.5 \times 10^{-2}$ sec.

The CIDEP results using the EFP model showed that for R.I. the quantity $P^\infty/\mathcal{F}$ was independent of k when $\Lambda > 10^{-3}$ although both P^∞ and $\mathcal{F}$ (as already discussed for CIDNP) were significantly altered. That is, Eq. (3.20) for EFA still applied provided $\Lambda > 10^{-3}$. [We will refer to the model of Section II and Eq. (2.40), where the exchange forces do not affect the diffusive trajectories, as the exchange forces absent (EFA) model.] This important result demonstrates that, to a large extent, the polarizations are independent of the details of the spin-selective chemical reaction, and they are just linearly dependent on $\mathcal{F}$. This, of course, means that in our models, where $\hbar J_0/kT \gg 1$ and the radical trapping (and reacting) region is around $r \sim d$, the region where polarization is developed lies where $r > d$ such that $\hbar J(r)/kT \gg 1$. This is precisely the feature which is included in a simple manner in the EFA model. But the actual values of $\mathcal{F}$ and P^∞ are very model sensitive.

However, for the smaller values of J_0 and k ($\Lambda < 10^{-3}$), the EFP and EFA results for $P^\infty/\mathcal{F}$ do *not* agree. In fact $P^\infty/\mathcal{F}$ and P^∞ for EFP change sign in some of the cases. This must be due to a new mechanism generating the polarization which no longer depends upon $\mathcal{F}$. When $\mathcal{F}$ is negligible, then the small differences in Boltzmann factors for singlets versus triplets in the polarization region (i.e., the time spent in a given region is different for singlets than for triplets) can have the effect of leading to a slight excess of singlets generating polarizations (this we call a relative diffusion model or RDM), which are negative in sign to the effects of the reaction which depletes singlets. But for our model, the RDM polarizations are much smaller than normal polarizations which arise from substantial values of $\mathcal{F}$, although $P^\infty/\mathcal{F}$ may be of the same order but of opposite sign. The RDM polarization becomes more important for faster diffusion and may yield very large values of $P^\infty/\mathcal{F}$ ($P^\infty/\mathcal{F} = -0.465$ for $D = 10^{-4}$ cm^2/sec, $J_0 = 10^{13}$ sec^{-1}, $Q = 10^8$ sec^{-1}, and $r_{ex} = d = 4$ Å). That the relations for the Λ dependence of the CIDNP quantities $\mathcal{F} - \mathcal{F}_0$ do not apply when $\Lambda < 10^{-3}$ may be similarly understood as being due to the RDM.

We have examined the time-evolved results for $P(N)$ where $r_N = 212$ Å in Pedersen and Freed.[9] For EFA we have of course $P(N) = 0$ at all times, while for EFP large polarizations are built up for short times (while the singlets are still effectively trapped), but eventually the singlets reach r_N and neutralize the large polarizations except for the small RDM polarizations. It is interesting to note that for $\hbar J_0 = 25kT$, the plateau value of $P(N) = 10.3 \times 10^{-3}$ is *precisely* the result which was obtained for $k \neq 0$ and $t \to \infty$ (for $\hbar J_0 = 10kT$, there is no clean plateau region, so the comparison is not as clear). This kind of agreement supports our use of the device of the kinetically irreversible reaction at $r = d$ to maintain the radical trapping, and it further shows that the $\mathcal{K}$-operator should only affect the diagonal singlet elements and not the off-diagonal elements. We note, however, that the lengths of time the singlets are trapped for EFP are surprisingly short considering the strengths of the trapping potential, which should lead to stable bond formation. This is undoubtedly due in part to the assumption of overdamping whereby momentum relaxation effectively occurs instantaneously (cf. Section IV, A).

6. *Nonspherical Radicals*

All the calculations have been performed for spherically-symmetric exchange interactions and spherical radicals for reasons of simplicity. Since most

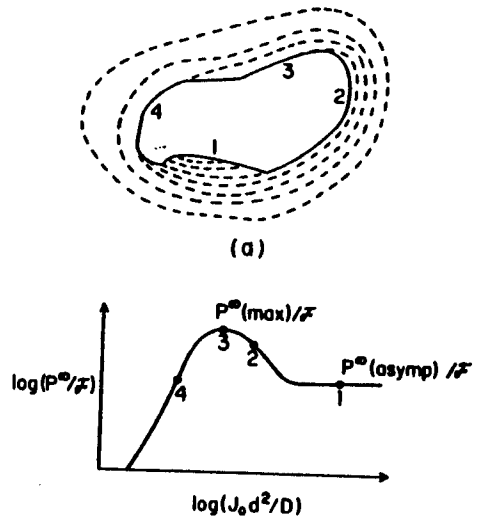


FIG. 8. Nonspherical radicals. (a) Suggested contours of constant J-value about a nonspherical radical interacting with a spherical radical. Spin-selective chemical reaction may occur only at region 1. (b) Typical variation of $P^{\infty}/\mathcal{F}$ with $J_0 d^2/D$ for spherical radicals showing suggested equivalent points corresponding to regions 1–4 in (a). [By permission from Pedersen and Freed.[7]]

interacting radicals will display anisotropic features in their exchange interactions and their ability to react, some comments on expected effects from nonspherical features are appropriate.

Suppose, for simplicity, we consider the interaction of a spherical radical (e.g., an H atom) with a highly nonspherical radical, with the latter represented in Fig. 8a. The solid curve represents the outer extent of the radical, while each of the dotted curves represents a contour of constant J value (e.g., J varies by a factor of 10 between adjacent curves). Suppose now a spin-selective chemcial reaction must first take place to initiate the spin-polarization process. This requires a region where $\hbar|J_0|/kT > 1$, and this region should have a large enough extension that vibrational relaxation to the bound state may occur. In Fig. 8a, only the region 1 is assumed to satisfy this condition. Thus the radicals must approach region 1, where a reaction may take place generating a net triplet character (symbolized by $\mathcal{F}$). If now we have $D \sim 10^{-5}$ cm^2/sec, so the polarization process is due to reencounters after moderate separations, then these reencounters may occur at different regions in Fig. 8a (e.g., regions labeled 1–4), each with its own characteristic range of values of J. In Fig. 8b we show the typical dependence of $P^{\infty}/\mathcal{F}$ on J_0 obtained for

spherical radicals with the results for regions 1–4 (as though they each represented the behavior of a different spherical molecule). (Also we are neglecting any effects from the orientation dependence of d and r_{ex} upon Qd^2/D and r_{ex}/d in our discussion.)

The main points to note now are: (1) $P^{\infty}/\mathcal{F}$ is independent of $\mathcal{F}$ for spherical radicals; (2) for a nonspherical radical, $\mathcal{F}$ may be greatly reduced by a geometric factor, but the resulting polarization $P^{\infty}/\mathcal{F}$ should still be essentially independent of $\mathcal{F}$; one only requires that the series of encounters, subsequent to each reactive encounter (e.g., at region 1 in Fig. 8a), be characterized by a very similar distribution in J values, as expected for our model of Fig. 8a. The resulting $P^{\infty}/\mathcal{F}$ will then be no greater than, but usually smaller than, $P^{\infty}(\max)/\mathcal{F}$ depending on the typical distribution of J values for the subsequent encounters. If the radical is nearly spherical, then a value close to $P^{\infty}(\text{asympt})/\mathcal{F}$ will result, and, if regions like 2 and 3 dominate, then a value closer to $P^{\infty}(\max)/\mathcal{F}$ will result.

7. *Quenching of Initial Polarization*

Typical results have been obtained for the effects of quenching of initial polarization.[7] EFA was utilized since (1) the off-diagonal elements ρ_{S,T_0} which are the important terms here are unaffected by the exchange forces and (2) the depolarization should occur in regions of $J_0 \sim D/d^2 \ll kT/\hbar$. The results for a contact exchange model, where $J(r_j) = J_0 \delta_{r_j, r_0}$, may be summarized by

$$\Delta P(d_i) \simeq \{(2J_0\tau_1)^2/[1 + 4(J_0^2 + Q^2)\tau_1^2]\}\,[1 - H(Qd^2/D, J_0 d^2/D)] \tag{4.49}$$

where τ_1 is given by Eq. (3.19).

When $H(Qd^2/D, Jd^2/D) = 0$, then Eq. (4.49) gives just the probability of Heisenberg spin-exchange per $(S\text{–}T_0)$ encounter that has been determined from relatively simple analytical solutions.[28] One finds that

$$H(Qd^2/D, J_0 d^2/D) \simeq h(Qd^2/D)/[1 + 4(J_0^2 + Q^2)\tau_1^2] \tag{4.50}$$

such that H is typically small compared to unity, but it may be approximated by $h \approx (Qd^2/D)^{\varepsilon''}$ $\varepsilon'' \sim \frac{1}{2}$ for $Qd^2/D < 0.16$. This extra term represents the effect of successive reencounters which tend to generate new polarizations, an effect which was not included in these earlier models.

Typical results for finite range of the exchange are given in ref. 9. The most significant difference from a contact exchange model is that for $J_0 > J_0(\max)$; it is possible to have $\Delta P(d_i) > 1$ representing the fact that the depolarization is completed at radical separations $> d$. For these large J_0 values, the results

[28] J. H. Freed, *J. Chem. Phys.* 45, 3452 (1966); M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *ibid.* 51, 2690 (1969); C. S. Johnson, *Mol. Phys.* 12, 25 (1967).

indicate that $\Delta P(d_1)$ varies approximately as

$$\Delta P(d_1) \simeq 1 + (\lambda d)^{-1} \ln[1 + (J_0 d^2/D)(\lambda d)^{-1}] \tag{4.51}$$

For small $J_0 < J_0(\max)$, one has a result very similar to Eq. (4.49)

$$\Delta P(d_1) \simeq (2J_0 \tau_1)^2 [1 - H'(Qd^2/D, J_0 d^2/D)] \tag{4.52}$$

where τ_1 is given by Eq. (3.15) and H' is very similar to H.

V. Further Models and Methods

A. Eigenfunction Expansion Methods

As an alternative to the finite difference methods employed extensively here, one may employ eigenfunction expansion methods in terms of modified Bessel functions as earlier noted. (The types of procedures involved are then similar to those used in Section VI for the initial triplet mechanism, but in that case orientational space is considered.) The appropriate modified Bessel functions are those which have the required reflecting wall at $r_0 = d$. These are known[29] and may be written for spherically symmetric problems as

$$f_0(ur) = -(r-d)(ur)^{-1}[1 + (ud)^{-2}]^{-1/2}\{uy_0[(r-d)u] - d^{-1}j_0[(r-d)u]\} \tag{5.1}$$

where

$$j_0[z] = \sin z/z \tag{5.2a}$$

and

$$y_0[z] = -\cos z/z \tag{5.2b}$$

are the spherical Bessel functions of the first and second kind with $\ell = 0$. Note that for $d = 0$, $f_0(ur) \to j_0(ur)$. More generally, the well-known Bessel function expansion in eigenfunctions

$$G_{\ell m}(\mathbf{u}, \mathbf{r}) = (2/\pi) j_\ell(ur) Y_\ell^m(\Omega), \tag{5.3}$$

where $Y_\ell^m(\Omega)$ are the spherical harmonics, is to be replaced by

$$\tilde{G}_{\ell m}(\mathbf{u}, \mathbf{r}) = \frac{2}{\pi} f_\ell(ur) Y_\ell^m(\Omega) \tag{5.4}$$

with

$$f_\ell(ur) = [j_\ell(ur) y_\ell'(ud) - y_\ell(ur) j_\ell'(ud)]/[j_\ell'(ud)^2 + y_\ell'(ud)^2]^{1/2} \tag{5.5}$$

where the primes imply derivatives (with respect to ur).[29]

[29] H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids." Oxford Univ. Press, London and New York, 1959.

Eigenfunction expansion methods for the solution of the SLE are illustrated in Section VI for a model involving rotational reorientation. The main difficulty with its use in the present case is the lack of reasonable "selection rules" for the "matrix elements" of (1) exchange interactions of the form Eq. (2.41) and (2) potentials $U(r)$ in Eq. (4.2) [as well as some problems with $\mathscr{H}(r)$]. However, perturbation approaches analogous to the one in Section VI, and valid for $J_0 \tau_1 \ll 1$ and $U(r) = 0$, may be reasonably carried out by these methods.[24,30]

We illustrate their utility in another context in the next section.

B. Finite Jump Diffusion

One may develop an analysis of jump diffusion by writing the master equation for the probability distribution $p(\mathbf{r}, t)$ as

$$\partial p(\mathbf{r}, t)/\partial t = (1/\tau) \int d^3R A(\mathbf{r} - \mathbf{R})\, p(\mathbf{r}, t) - (1/\tau)\, p(\mathbf{r}, t) \tag{5.6}$$

where $A(\mathbf{r} - \mathbf{R})$ is the probability that a molecule jumps to position $\mathbf{r}$ from position $\mathbf{R}$ in a single step. Thus

$$\int A(\mathbf{r} - \mathbf{R}) d^3R = 1. \tag{5.7}$$

Also τ is the mean time between successive jumps. Let us introduce, by analogy to Eq. (2.8),

$$p(r, t) \equiv (1/4\pi) \int\int p(\mathbf{r}, t) \sin\theta \, d\theta \, d\phi, \tag{5.8}$$

and introduce $A[\rho]$ as the Fourier transform of $A(\mathbf{r})$:

$$A(\boldsymbol{\rho}) = \int A(\mathbf{r}) e^{i\boldsymbol{\rho}\cdot\mathbf{r}} d^3r. \tag{5.9}$$

This is the model used by Torrey,[31] for which the solution is

$$p(\mathbf{r}, t) = (1/2\pi)^3 \int \exp\{-i\mathbf{r}\cdot\boldsymbol{\rho} - (t/\tau)[1 - A(\boldsymbol{\rho})]\}\, d^3\rho. \tag{5.10}$$

[30] G. T. Evans, P. D. Flemming, and R. G. Lawler [*J. Chem. Phys.* 58, 2071 (1973)] have studied a stochastic Liouville solution for a simplified model in terms of the simple Bessel function expansion, Eq. (5.3) for $\ell = 0$; i.e., they neglect to consider the boundary condition at $r = d$. They also employ delta function representations of $J(r)$ and $\mathscr{H}(r)$, but such a model fails even to reproduce many of the important qualitative features of the results for CIDEP given in Section III. Their results for CIDNP are more useful in the limit of small $J(r)$, but their treatment would be improved by the use of Eq. (5.1) instead of Eq. (5.3), i.e., with a proper boundary condition.

[31] H. C. Torrey, *Phys. Rev.* 92, 962 (1953).

We now rewrite the first term on the right-hand side of Eq. (5.6) as

$$\int d^3R A(\mathbf{r}-\mathbf{R})\, p(\mathbf{R},t)$$

$$= (1/2\pi)^6 \int d^3R \int d^3\rho \int d^3k e^{i\rho\cdot(\mathbf{r}-\mathbf{R})} A(\rho)\, e^{[ik\cdot R-(t/\tau)[1-A(k)]]}. \tag{5.11}$$

For simplicity, one now assumes isotropic diffusion so that $A(\rho)$ depends only on the magnitude of ρ, i.e.,

$$A(\rho) = A(\rho). \tag{5.12}$$

Then one may use the usual spherical Bessel function expansion of $e^{i\rho\cdot r}$, as well as the addition formula for the Legendre polynomials and the orthonormal properties of the latter, to obtain

$$(2/\pi)\int_0^\infty R^2\, dR \int_0^\infty \rho^2\, d\rho A(\rho)\, j_0(\rho R)\, j_0(\rho r)\, p(R,t)/4\pi \tag{5.13}$$

for the first term on the right-hand side of Eq. (5.6). Now one may let

$$A(\rho) = 1/(1+D\tau\rho^2) \tag{5.14a}$$

which corresponds to a model in which

$$A(r) = [4\pi D\tau r]^{-1} \exp[-r/(D\tau)^{1/2}] \tag{5.14b}$$

and $D\tau = \langle r^2\rangle/6$, where $\langle r^2\rangle$ is the mean square jump distance. For the current application in relative diffusion, $D = D_a + D_b$ and r is the separation. When this form of $A(\rho)$ is used and the integrations of Eq. (5.8) are employed in Eq. (5.6), one obtains

$$\partial p(r,t)/\partial t = (1/\tau)\int_0^\infty (D\tau)^{-1/2}(R/r)$$

$$\times \tfrac{1}{2}\{\exp[-|R-r|/(D\tau)^{1/2}] - \exp[-|R+r|/(D\tau)^{1/2}]\}$$

$$\times p(R,t)\, dR - (1/\tau)\, p(r,t). \tag{5.15}$$

This expression can then be employed for the finite-difference approach to obtain a W-matrix for jumps of finite size.

Now Eq. (5.15) is the appropriate expression when r may vary from 0 to ∞; thus Eq. (5.15) conserves total probability in this space. For real situations, one must restrict the range of r from d to ∞. In this restricted space one must introduce the modified spherical Bessel functions f_n in place of the j_n, i.e., Eq. (5.13) becomes

$$(2/\pi)\int_d^\infty R^2\, dR \int_0^\infty \rho^2\, d\rho A(\rho)\, f_0(\rho R)\, f_0(\rho r)\, p(R,t)/4\pi. \tag{5.13'}$$

One then obtains, instead of Eq. (5.15),

$$\partial p(r,t)/\partial t = (1/\tau)\int_d^\infty dR[d^2 - D\tau]^{-1}(R/r)$$

$$\times \tfrac{1}{2}\{[d^2(D\tau)^{-1/2} - (D\tau)^{1/2}]\exp[-|R-r|/(D\tau)^{1/2}]$$

$$+ [d(D\tau)^{-1/4} - (D\tau)^{1/4}]^2 \exp[-(R+r-2d)/(D\tau)^{1/2}]\}$$

$$\times p(R,t) - (1/\tau)\, p(r,t). \tag{5.15'}$$

Equation (5.15') may be shown to satisfy the conservation of total probability in the space from d to ∞. Thus it implicitly includes the reflecting wall at $r_0 = d$.[32]

The problem of the introduction of potential functions into the jump diffusion is a complex one. We note that, in general, one may replace $(1/\tau)A(\mathbf{r}-\mathbf{R})$ in Eq. (5.6) by $B(\mathbf{r}-\mathbf{R})$ such that

$$B(\mathbf{r}-\mathbf{R}) = \tau^{-1}A(\mathbf{r}-\mathbf{R})e^{-U(r)/kT}/X(\mathbf{r},\mathbf{R}) \tag{5.16}$$

where $X(\mathbf{r},\mathbf{R})$ is a symmetric function in $\mathbf{r}$ and $\mathbf{R}$ [i.e., $X(\mathbf{r},\mathbf{R}) = X(\mathbf{R},\mathbf{r})$], but is otherwise dependent upon the microscopic details of the model. Note that $B(\mathbf{r}-\mathbf{R})$, the jump *rate* from $\mathbf{R}$ to $\mathbf{r}$, obeys detailed balance, and it is written in a manner which recognizes that, in general, τ has lost its simple physical meaning (i.e., a mean jump time is now a function of $\mathbf{r}$ and $\mathbf{R}$). A simple first guess would be to let $X(\mathbf{r},\mathbf{R}) = 1$ even though its physical implications are not at all clear.

C. Inertial Effects

One of the most serious weaknesses of the self-consistent or EFP Method of Section IV, E from the point of view of reactive dynamics in liquids is the fact that the use of the Smoluchowski equation implies instantaneous relaxation of the momentum; i.e., if β is the friction coefficient, one is essentially letting $\beta \to \infty$ while $D = kT/\mu\beta$ where μ is an appropriate reduced mass; (this is actually a coarse-graining in time assumption). Also, one is considering the valence forces $\mathbf{F}$ to be overdamped; i.e., one is assuming $|\mathrm{div}\,\mathbf{F}| \ll \mu\beta^2$. One can, of course, formulate the SLE in the combined configuration and momentum phase space of the two particles (i.e., a twelve-dimensional diffusion problem). However, if the two particles are similar, such that $\beta_1 = \beta_2 = \beta$, and the forces between them depend only on their relative coordinates, then it is possible to separate out the center mass diffusion and relative diffusion, where $\mu = m_1 m_2/(m_1+m_2)$. One then has for the relative

[32] We wish to thank Dr. L. P. Hwang for obtaining these results.

diffusion in place of Eq. (4.1)[33]:

$$\Gamma_{r,u}\, p(\mathbf{r},\mathbf{u}) = -\mathbf{u}\cdot\nabla_r p + \mu^{-1}[\nabla_r U(\mathbf{r})]\cdot\nabla_u p + \beta\nabla_u\cdot(\mathbf{u}\cdot\mathbf{p}) + q\nabla_u^2 p \tag{5.17}$$

where $q = \beta kT/\mu$ and $\mathbf{r}$ and $\mathbf{u}$ are the relative coordinates and velocities (i.e., a six-dimensional problem). (Of course, if $m_1 \gg m_2$ one can treat the motion of particle 2 relative to the fixed particle 1.) Also in Eq. (5.17) we have neglected cross-damping coefficients $\beta_{1,2}$ for simplicity, but they can easily be included.[21a]

If now the relative force $F(\mathbf{r}) = F(r)$, i.e., a central force, and isotropic space is assumed, then the appropriate symmetry considerations allow one to reduce the problem to just three dimensions: $|\mathbf{r}| = r$, $|\mathbf{u}| = u$, and essentially $\cos\theta = \mathbf{r}\cdot\mathbf{u}$. The solution of the resulting SLE is in many ways similar to that already discussed for "inertial effects" in orientational relaxation,[34] and it would be too lengthy to elaborate here. However, we note that the most effective method of solution in the present case is expected to be a combination of the finite-difference method in the variable r, with eigenfunction expansion techniques applied to u as well as the relevant angles in a coupled representation.

One should note that the inclusion of "inertial effects" will also allow one to specify initial conditions of the radical pair just after cleavage such that $u \neq 0$, so that initial separations may be achieved quite naturally. Also, the variation of $J(r)$ in $\mathscr{H}$ by means of the relative diffusion may show substantial inertial effects, because of the rapid variation of $J(r)$ with r.

D. Generalized Fokker–Planck Theory

It is not necessary to be satisfied with Brownian motion models of the liquid state reactive dynamics. One may, under very general conditions, replace Eq. (5.17) by a generalized (time-dependent) Fokker–Planck operator for the relative diffusion, including spin, which is a rigorous many-body solution to this semiclassical problem.[21a] One then obtains a time-dependent friction coefficient $\beta(t)$, for which a variety of memory-function approximations may be employed,[21a] in an effort to better approximate the motion.

E. Orientation-Dependent Reaction Kinetics

When either $\mathscr{K}(\mathbf{r}_1,\mathbf{r}_2)$ or $U(\mathbf{r}_1,\mathbf{r}_2)$ in Eqs. (2.1) or (4.1) depend upon the orientations of the two particles, the rotational diffusion of these particles becomes important. One may then generalize Eqs. (2.1) or (2.4) to deal with this feature by a composite of techniques used here for the r variable and

[33] S. Chandrasekhar [*Rev. Mod. Phys.* 15, 1 (1943)] gives the single particle expressions.
[34] G. V. Bruno and J. H. Freed, *J. Phys. Chem.* 78, 935 (1974).

eigenfunction expansion approaches similar to that used by Stockmayer *et al.*[35] for classical diffusion. We have already indicated, in a qualitative way, the kinds of effects one might expect for CIDNP and CIDEP due to rotations of nonspherical molecules.

VI. The Triplet Mechanism for CIDEP

A. General Considerations

Wong *et al.*[13] have presented a theory for CIDEP polarization for some photochemical processes in liquid solution. The model adopted by Wong *et al.* is based upon polarizations generated by the intersystem crossing of a photoexcited singlet state to a triplet state such that one (or more) of the molecular frame triplet states $T_{x'}$, $T_{y'}$, or $T_{z'}$ is initally populated preferentially. This, in itself, is a commonly observed phenomenon in the solid state. They showed that this preferential population, coupled with the effect of the zero-field splitting term in modifying the high-field triplet states, can lead to a rotationally invariant term causing a net initial polarization of the radical pair which emanates from the reaction (or decomposition) of the triplet molecule. The crucial requirement then appears to be that the triplet lifetime be short compared to the triplet spin-lattice relaxation time T_1, so that this initial polarization is not relaxed before the radical pair forms.

This mechanism has now been invoked in several experimental CIDEP studies of photolytically generated radicals to explain pure emission spectra as well as cases where both radicals are observed in emission.[36,37] An important feature of this mechanism is that it is essentially independent of the hyperfine terms and that it gives identical polarization for the two radicals, unlike the RPM. The likelihood of having both the triplet polarization mechanism of Wong *et al.* and the radical-pair mechanism contributing to the CIDEP polarization in such cases has been suggested by these workers.[36-38]

The theoretical treatment of Wong *et al.*[13] clearly demonstrates the potential importance of this photolytic triplet mechanism, for systems where the rate of triplet decomposition into a radical pair is rapid. However, they did not explicitly consider the dynamics of the problem, i.e., the dynamical competition between the rotational reorientation, the various triplet decay processes, and the T_1 process. In particular, the T_1 process is itself expected to be generated by the rotational modulation of the zero-field splitting. This

[35] K. Šole and W. H. Stockmayer, *J. Chem. Phys.* 54, 2981 (1971).
[36] S. K. Wong and J. K. S. Wan, *J. Amer. Chem. Soc.* 94, 7197 (1972); S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *ibid.* 95, 622 (1973); *Can. J. Chem.* 52, 251 (1974).
[37] P. W. Atkins, A. J. Dobbs, G. T. Evans, K. A. McLaughlan, and P. W. Percival, *Mol. Phys.* 27, 769 (1974).
[38] J. B. Pedersen, C. E. M. Hansen, H. Parbo, and L. T. Muus, *J. Chem. Phys.* 63, 2398 (1975).

is, in fact, a well-known mechanism. However, when the zero-field splitting becomes comparable to or larger than the tumbling rate, then, in general, the usual motional narrowing predictions break down, since one is in the "slow-motional" region. In this region there need no longer be a simple T_1 behavior. Instead the nonequilibrium polarizations will decay with several decay constants representing a more complex solution of the coupling of the spin-degrees of freedom to the reorientational process.[4] Despite the complexity of the problem, a thorough analysis may be given in terms of the SLE.

The analysis may be developed in terms of the excited triplet spin distribution represented by the spin-density matrix $\rho(\Omega, t)$. First one must make the fundamental assumption, essentially equivalent to that of Wong *et al.*, that a radical pair formed at time t either from the decomposition of an excited triplet molecule or from a reaction [e.g., abstraction of an electron (or an H atom) from a solvent molecule] will still be characterized by the same triplet spin-density distribution $\rho(t)$, although the *orbital* electronic distribution has been altered. This appears reasonable for a decomposition process. For an abstraction process, e.g., of a hydrogen atom, the electron spin (h_1) of the H atom must pair up with one of the original electrons (e_1) forming the triplet, so the other electron (h_2) of the pair bond of the H atom in its original solvent molecule will have the same spin character as e_1. Once we adopt this point of view, then we note that the polarization of each radical product is given by [cf. Eq. (2.15)]

$$P = \rho_{T_-T_-} - \rho_{T_+T_+} \tag{6.1}$$

where we have set $\rho_{ST_0} = 0$, since we have assumed that the excited state from which the reaction takes place is a simple triplet state. Actually, one needs the polarization achieved after the process is completed, by which the initially excited triplet molecules have formed a radical pair, or relaxed to a stable ground state, or else decomposed to yield other products. The polarization of the radical products in this limit is given by[39a]

$$\mathscr{P}P^{\infty} \equiv \lim_{t\to\infty} P(t) = \int_0^{\infty} [\rho_{T_-T_-}(t) - \rho_{T_+T_+}(t)]\, k_1\, dt \tag{6.2}$$

or, alternatively,

$$\mathscr{P}P^{\infty} = \hat{k}_1 [\rho_{T_-T_-}(s=0) - \rho_{T_+T_+}(s=0)] \tag{6.3}$$

where $\hat{k}_1$ is the pseudo-first-order rate constant for formation of the radical pair from the triplet states. We again use the $t \to \infty$ limit on the assumption

[39a] The equations in this section thus differ slightly from the equivalent expressions in Ref. 16. To bring the results in Ref. 16 into correspondence with the notation used here, one should replace P^{∞} in that reference by $\mathscr{P}P^{\infty}$, where $\mathscr{P} = k_1/\hat{k}$, but P_{eq} is unchanged.

that the polarization generating process is much faster than any subsequent rate processes of the separated radical pair, e.g., their spin relaxation and their further reactivity, and the expressions are defined so P^{∞} is the normalized polarization of only those triplets which form the radical pair.[39a]

For this problem the SLE is

$$\partial\rho/\partial t = -i\mathscr{H}^{\times}\rho - \Gamma(\rho - \rho_{eq}) - (\hat{k}_1 + \hat{k}_2)\rho \tag{6.4}$$

where $\hat{k}_2$ is a quasi-first-order rate constant for all other processes which deplete the triplets, and Γ is the Markovian operator for the classical molecular tumbling process. Also, ρ_{eq} is the equilibrium density matrix given by

$$\rho_{eq} = \sigma \exp(-\hbar\mathscr{H}/k_B T)/\mathrm{Tr}\exp(-\hbar\mathscr{H}/k_B T) \simeq (\sigma/3)(1 - \hbar\mathscr{H}/k_B T) \tag{6.5}$$

where the approximate equality is the usual high temperature approximation and σ is discussed below. The inclusion of ρ_{eq} in Eq. (6.4) guarantees that the spins relax to thermal equilibrium. (It was not necessary for the RPM, because S and T_0 states have the same Zeeman energy, and the effects of the exchange energy were included as given in Section IV.) As a result of the dissociation and decay processes (assumed spin-independent), ρ_{eq} obeys the simple rate equation

$$\partial\rho_{eq}/\partial t = -(\hat{k}_1 + \hat{k}_2)\rho_{eq}. \tag{6.6}$$

It is convenient, at this stage, to introduce the variable χ which is the deviation of ρ from its equilibrium value:

$$\chi \equiv \rho - \rho_{eq}. \tag{6.7}$$

It then follows from Eqs. (6.4) and (6.6), that χ obeys

$$\partial\chi/\partial t = -[i\mathscr{H}^{\times} + \Gamma + \hat{k}]\chi \tag{6.8}$$

where we have let

$$\hat{k} \equiv \hat{k}_1 + \hat{k}_2. \tag{6.8a}$$

Equations (6.6)–(6.8) are seen to yield the formal solution

$$\rho(t) = e^{-\hat{k}t}[e^{-(i\mathscr{H}^{\times} + \Gamma)t}\chi(t=0) + \rho_{eq}(t=0)]. \tag{6.9}$$

We now normalize $\rho(t=0) \equiv \rho(0)$ and $\rho_{eq}(t=0) \equiv \rho_{eq}(0)$, so that

$$\mathrm{Tr}\,\rho(0) = \mathrm{Tr}\,\rho_{eq}(0) = 1 \tag{6.10a}$$

and, more generally,

$$\mathrm{Tr}\,\rho_{eq}(t) = \mathrm{Tr}\,\rho(t) \equiv \sigma(t) \tag{6.10b}$$

and

$$\mathrm{Tr}\,\chi(t) = 0 \tag{6.10c}$$

where $\sigma(t)$ obeys the same rate equation as ρ_{eq} in Eq. (6.6), i.e., it measures the fraction of excited triplet molecules which remain at time t.

The Laplace transforms of Eqs. (6.6) and (6.8) are

$$[s+k]\rho_{eq}(s) = \rho_{eq}(0) \tag{6.11a}$$

and

$$[(s+\hat{k}) + i\mathscr{H}^{\times} + \Gamma]\chi(s) = \chi(0) \tag{6.11b}$$

and we have

$$\rho(s) = \chi(s) + \rho_{eq}(s). \tag{6.12}$$

Then in the limit $s \to 0$ required for Eq. (6.3), we have

$$\lim_{s'\to\hat{k}} \rho(s') = \lim_{s'\to\hat{k}} \chi(s') + \rho_{eq}(0)/\hat{k} \tag{6.13}$$

where $s' = s+\hat{k}$. Thus we may solve for $\chi(s')$ and add to it the second term of Eq. (6.13).

In the present problem $\mathscr{H}(\Omega)$ is the orientation-dependent triplet spin-Hamiltonian[39b]:

$$\mathscr{H} = \omega_0 S_z + \sum_{m'} \{6^{-1/2} D\mathscr{D}^2_{0,m'}(\Omega) + (E/2)[\mathscr{D}^2_{0,m'}(\Omega) + \mathscr{D}^2_{-2,m'}(\Omega)]\} A^{2,m'} \tag{6.14}$$

where

$$A^{2,0} = 6^{1/2}(S_z^2 - \tfrac{1}{3}S^2), \tag{6.15a}$$

$$A^{2,\pm 1} = \mp(S_\pm S_z + S_z S_\pm), \tag{6.15b}$$

$$A^{2,\pm 2} = S_\pm^2.$$

Here D and E are the standard zero-field splitting parameters, ω_0 is the Larmor frequency for the triplet, Ω represents the Euler angles for the transformation between molecular axes x', y', z' and space-fixed axes (x, y, z), $\mathscr{D}^L_{KM}(\Omega)$ are the generalized spherical harmonics, and Γ_Ω is the Markovian operator for the rotational reorientation process. For isotropic reorientation, the eigenfunctions of Γ_Ω are the $\mathscr{D}^L_{KM}(\Omega)$ with eigenvalues

$$E_{L,K,M} = RB_L L(L+1) \tag{6.16}$$

where R is the isotropic rotational diffusion coefficient and B_L is a "model parameter," which is unity for Brownian reorientation, and at the other limit of strong jumps (leading to randomization of orientation with each molecular collision) one has $B_L = R/E_{L,K,M}$ for $L \neq 0$. A whole range of jump models

[39b] J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Chem. Phys.* **55**, 5270 (1971). The $\mathscr{D}^L_{KM}(\Omega)$ utilized are in the notation of J. H. Freed and G. K. Fraenkel [*J. Chem. Phys.* **39**, 326 (1963)].

between these two cases may be treated in terms of the proper B_L as discussed elsewhere,[4,40] and anisotropic motion may also be treated in the standard manner.[4,40]

B. Solution and Results

The method of solution of Eq. (6.11b) is to expand $\chi(s')$ in the complete orthogonal set $\mathscr{D}^L_{KM}(\Omega)$ as

$$\chi(s') = -i \sum_{LKM} C^L_{KM}(s')\mathscr{D}^L_{KM}(\Omega). \tag{6.17}$$

Also, one can expand the initial condition (see below) as

$$\chi(t=0) = -i \sum_{LKM} d^L_{KM}\mathscr{D}^L_{KM}(\Omega). \tag{6.18}$$

One can rewrite Eq. (6.11b) as a matrix equation[39] using Eqs. (6.17) and (6.18), and by taking spin-matrix elements of C^L_{km} and d^L_{km} as described [illegible]. One has

$$\mathscr{A}\mathbf{C} = \mathbf{d} \tag{6.19}$$

where $\mathbf{C}$ is an n-dimensional column vector consisting of the expansion coefficients $C^L_{KM}(i)$, while $\mathbf{d}$ is the n-dimensional column vector of $d^L_{KM}(i)$'s (see below) and $\mathscr{A}$ is an $n \times n$-dimensional complex matrix, obtained from evaluating the operator coefficient of $\chi(s')$ in Eq. (6.11b) in the standard manner.[39b]

At this stage we note that for the $\mathscr{H}(\Omega)$ of Eq. (6.10) and Γ_Ω with eigenvalues of Eq. (6.16), $\mathscr{A}$ is formally *identical* to the matrix required to solve triplet slow-tumbling spectra when rf and dc fields are parallel, and this has already been given by Freed *et al.*[39b] (one only requires $i\omega \to s'$).

Next we note that for isotropic liquids one wants the average $\bar{\rho}(s')$ given by

$$\bar{\rho}(s') = (1/8\pi^2)\int d\Omega\rho(s')$$

$$= -iC^0_{0,0}(s') + \tfrac{1}{3}(1 - \hbar\omega_0 S_z/k_B T)/s' \tag{6.20}$$

where the second equality follows from Eqs. (6.12), (6.18), (6.11a), (6.5), and (6.14).

[40] S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.* **56**, 716 (1972). The jump diffusion model used here is based on Ivanov's model [E. N. Ivanov, *Sov. Phys.—JETP* **18**, 1041 (1964); also K. A. Valiev and E. N. Ivanov, *Sov. Phys.—Usp.* **16**, 1 (1973)], where one recognizes that the conditional probability function of Ivanov is the standard expansion in eigenfunctions of the appropriate Γ_Ω for jump diffusion. This matter is discussed in more detail by R. I. Cukier and K. Lakatos-Lindenberg [*J. Chem. Phys.* **57**, 3427 (1972)].

Also we note that the L, K, Mth element of $\mathbf{d}$ is given by

$$i\int d\Omega\rho(0)\mathscr{D}^{L}_{KM}{}^{*}(\Omega) = d^{L}_{KM}. \tag{6.21}$$

Note that $C^{L}_{K,M}(s')$ is still a spin-operator, as is $d^{L}_{KM}(i)$. Thus one must solve for

$$-i[\langle 1|C^{0}_{0,0}(s)|1\rangle - \langle -1|C^{0}_{0,0}(s)|-1\rangle] + P_{eq}/k \tag{6.22}$$

with

$$P_{eq} = \tfrac{1}{3}\hbar\omega_0/k_B T. \tag{6.23}$$

It is easy to show from the general properties of the expansion coefficients (cf. Freed *et al.*[39b]) that the diagonal elements of $C^{0}_{0,0}$ are pure imaginary. Thus one obtains

$$P^{\infty} - P_{eq} = \hat{k}\lim_{s'\to k}\mathrm{Im}[\langle -1|C^{0}_{0,0}(s)|-1\rangle - \langle +1|C^{0}_{0,0}(s)|+1\rangle]. \tag{6.24}$$

In Eqs. (6.22) and (6.24) we have employed conventional bra-ket notation for the diagonal matrix elements for $T_{\pm 1}$ in the laboratory frame.

1. *Initial Conditions*

We now consider the n-dimensional vector $\mathbf{d}$ with elements given by Eq. (6.21). We note that just after a preferential intersystem crossing, $\rho(0)$ is most conveniently described in the molecular frame. In general, one may write

$$\rho(0) = w_{x'}|X'\rangle\langle X'| + w_{y'}|Y'\rangle\langle Y'| + w_{z'}|Z'\rangle\langle Z'| \tag{6.25}$$

where $|X'\rangle$, $|Y'\rangle$, and $|Z'\rangle$ are the zero-field kets for the triplet in the molecular frame (i.e., $T_{x'}$, $T_{y'}$, and $T_{z'}$) and $w_{x'}$, $w_{y'}$, $w_{z'}$ are the preferential probabilities of populating these states by the intersystem crossing, such that

$$w_{x'} + w_{y'} + w_{z'} = 1. \tag{6.26}$$

[Equation (6.25) neglects any coherence between the relative probabilities of populating the three triplet states; otherwise $\rho(0)$ would have off-diagonal elements in the $|X'\rangle$, $|Y'\rangle$, $|Z'\rangle$ representation.] If we let $|m\rangle$, where $m = +1, 0$, or -1, represent the high-field kets in the molecular frame, then we have

$$|\pm 1\rangle = (\mp 1/2^{1/2})[|X'\rangle \pm i|Y'\rangle] \tag{6.27}$$

and these kets are the irreducible tensor components.[39b] The high-field kets in the molecular frame are transformed into the high-field kets in the laboratory frame $|k\rangle$ according to

$$|m\rangle = \sum_{k}|k\rangle\mathscr{D}^{1}_{mk}(\Omega) \tag{6.28}$$

with the generalized spherical harmonics already discussed. Thus

$$|m\rangle\langle m'| = \sum_{k,k'}|k\rangle\langle k'|\mathscr{D}^{1}_{mk}(\Omega)\mathscr{D}^{1}_{-m'-k'}(\Omega)(-1)^{m'-k'} \tag{6.29}$$

and one may transform Eq. (6.25) for $\rho(0)$ in the $|X'\rangle$, $|Y'\rangle$, $|Z'\rangle$ basis set into the $|k\rangle$ basis set. The matrix elements $d^{L}_{KM}(i)$, according to the definitions analogous to Eq. (6.22), appear in Pedersen and Freed[9] for an axially symmetric molecule (i.e., $E = 0$). In general one only has $L = 0$, or spherically symmetric, and $L = 2$ contributions, and only the $L = 2$ contributions will yield an effective CIDEP polarization mechanism. It is seen that the initial conditions corresponding to $|X'\rangle$ or $|Y'\rangle$ give identical results, since for E = 0, the choice of these molecular axes is arbitrary. Also they yield values for $d^{L}_{0M}(i)$ which are $(-\frac{1}{2})$ those for the initial condition of $|Z'\rangle$. Thus, it is sufficient to solve for the initial case of $\rho(0) = |Z'\rangle\langle Z'|$ and multiply the result by $r = [w_{z'} - \frac{1}{2}(w_{x'} + w_{y'})]$ to obtain the correct P^{∞} for an arbitrary initial condition.

2. *Perturbation Theory*

One can solve Eq. (6.19), subject to the initial conditions, by a perturbation method valid for small enough D. However, in zero-order, $\langle 1|C^{0}_{0,0}|1\rangle$ and $\langle -1|C^{0}_{0,0}|-1\rangle$ in Eq. (6.24) are "degenerate" with $\langle 0|C^{0}_{0,0}|0\rangle$, so degenerate perturbation theory is called for with a van-Vleck-type transformation being appropriate.[9]

We summarize the procedure by introducing three transformations **U**, **T**, and **P** such that Eq. (6.19) becomes

$$(\mathbf{PTU}\mathscr{A}\mathbf{U}^{-1}\mathbf{T}^{-1}\mathbf{P}^{-1})(\mathbf{PTUC}) = (\mathbf{PTUd}) \tag{6.30}$$

or

$$\mathscr{A}'''\mathbf{C}''' = \mathbf{d}'''.$$

Here **U** is the orthogonal transformation which transforms the diagonal matrix elements of $C^{0}_{0,0}(i)$ into their "normal modes" of relaxation. **T** is a symmetrizing transformation,[9] and **P** is the van-Vleck-type matrix which diagonalizes $\mathscr{A}'' \equiv \mathbf{TU}\mathscr{A}\mathbf{U}^{-1}\mathbf{T}^{-1}$ to lowest order in D. Once this approximate diagonalization is achieved, then one solves for

$$(1/2^{1/2})[\langle -1|C^{0}_{0,0}|-1\rangle - \langle 1|C^{0}_{0,0}|1\rangle].$$

The final result of the perturbation analysis (for $E = 0$) yields

$$\frac{P'^{\infty}}{r} = \frac{4D}{15}\left\{\frac{\omega_0}{\omega_0^2+\tau_R^{-2}}\left[\frac{\hat{k}}{\hat{k}+T_1^{-1}} - \frac{(\hat{k}+2\tau_R^{-1})\hat{k}}{\omega_0^2+(\hat{k}+\tau_R^{-1})^2}\right] + \frac{4\omega_0}{4\omega_0^2+\tau_R^{-2}}\left[\frac{\hat{k}}{\hat{k}+T_1^{-1}} - \frac{(\hat{k}+2\tau_R^{-1})\hat{k}}{4\omega_0^2+(\hat{k}+\tau_R^{-1})^2}\right]\right\} \tag{6.31}$$

where $\tau_R = (6R)^{-1}$,

$$r = [w_{z'} - \tfrac{1}{2}(w_{x'} + w_{y'}) - (D/2\omega_0)P_{eq}], \tag{6.32}$$

$$T_1^{-1} = \frac{2}{15}D^2\left[\frac{\tau_R^{-1}}{\omega_0^2+\tau_R^{-2}} + \frac{4\tau_R^{-1}}{(2\omega_0)^2+\tau_R^{-2}}\right], \tag{6.33}$$

and

$$P^{\infty} = P'^{\infty} + [T_1^{-1}/(\hat{k}+T_1^{-1})]\,P_{eq}. \tag{6.34}$$

(We will generally use P'^{∞} to represent that part of the polarization which is independent of P_{eq} terms.) Also the presumed validity of the analysis requires

$$D^2 \ll (\omega_0^2+\tau_R^{-2}). \tag{6.35}$$

Note that the T_1 of Eq. (6.33) is the well-known result for triplets, but its validity in the present derivation requires only that Eq. (6.35) be fulfilled. Atkins and Evans[15] have obtained a very similar result from a different approximate analysis. In the limits

$$\omega_0 \gg \tau_R^{-1} \gtrsim \hat{k} \gg T_1^{-1} \simeq (4/15)(D^2/\omega_0^2)\tau_R^{-1} \tag{6.36}$$

one has the simple result

$$P'^{\infty}/r \to (8D/15\omega_0) \tag{6.37}$$

which is seen to be equivalent to the perturbation result of Wong *et al.* (for $\hat{k}_1 \gg \hat{k}_2$) wherein the dynamical features are unimportant.[13] It immediately indicates that substantial polarizations can be generated in that limit. The positive (negative) sign in Eq. (6.34) or (6.31) indicates absorptive (emissive) polarization.

The dependence of P'^{∞} upon $\hat{k}_1$ given in Eq. (6.31) is an interesting one. It is seen that P'^{∞} goes to zero both for very small and very large values of $\hat{k}_1$. That it goes to zero for small $\hat{k}_1$ follows because any initial polarization is quenched by the T_1 process before the triplet reacts to give a radical pair. That it goes to zero for large $\hat{k}_1$ represents the fact that the initial population difference $(\rho_{T_-T_-}-\rho_{T_+T_+})$ immediately after a preferential intersystem crossing is zero since only the isotropic contributions to $\rho(0)$ are important [cf. Eq. (6.20)]. The polarization is generated only in times of the order of τ_R, as the rotational averaging effectively mixes in the anisotropic contributions from $\rho(0)$ into the polarization (which is an isotropic average over all orientations).

The contribution of P_{eq} in Eq. (6.34) represents the competition between the triplet decomposition process and the T_1 process, going to zero for $\hat{k} \gg T_1^{-1}$ and P_{eq} for $T_1^{-1} \gg \hat{k}$.

We have compared Eq. (6.31) with the complete computer solutions, and we have found as a practical guide that it gives an adequate representation (to within 10% or better) provided

$$D^2 \lesssim \tfrac{1}{2}[\omega_0^2+\tau_R^{-2}]. \tag{6.38}$$

We illustrate the cases for large $D = 3000$ G for both large and small ω_0 in Figs. 9 and 10 for Brownian motion ($B_L = 1$). The results for $\omega_0 = 3000$ G

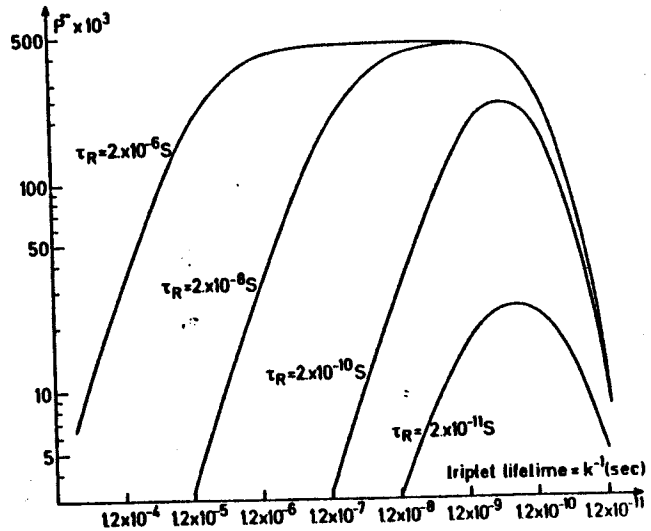


FIG. 9. Graph of P^{∞} vs triplet lifetime $= \hat{k}^{-1}$ for different values of τ_R the rotational correlation time. The zero-field splitting $D = 3000$ G, while $\omega_0 = 3000$ G. It is assumed that $\hat{k} = \hat{k}_1$; for $\hat{k} \neq 1$ these results should be multiplied by $\hat{k}_1/\hat{k}$ and the ordinate yields $\mathcal{P}P^{\infty}$. The initial condition $\rho(0) = |Z\rangle\langle Z|$ is assumed, so in general the results should be multiplied by r defined by Eq. (6.32). The results given do not include any contributions from P_{eq} [i.e., they are rigorously the P'^{∞} values, e.g., Eq. (6.34)]. [By permission from Pedersen and Freed.[16]]

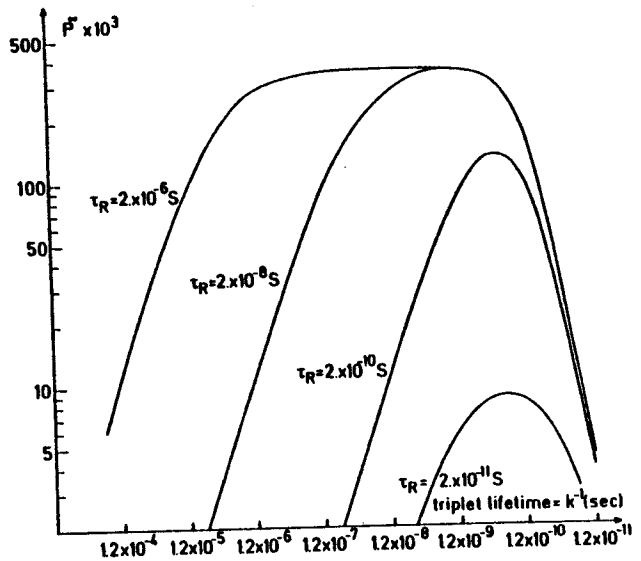


FIG. 10. Same as Fig. 9 but with $\omega_0 = 1000$ G. [By permission from Pedersen and Freed.[16]]

are generally in good agreement with Eq. (6.31), but for $\omega_0 = 1000$ G it is found that Eq. (6.31) breaks down. (These results may be scaled with the dimensionless parameters: ω_0/D, τ_R^{-1}/D, and k/D.) It is clearly seen from Figs. 9 and 10 that limiting values of P'^{∞} as high as 450×10^{-3} can be predicted for a range of $\hat{k}/D$ values and slow tumbling (while $P_{eq} \sim 10^{-3}$). More rapid tumbling acts to decrease P'^{∞}. When the tumbling is slow, substantial deviations are found between the exact solution and Eq. (6.31) for $\omega_0/D < 1$. Equation (6.31) tends to overestimate P'^{∞} in this case. In the slow-tumbling limit, one does not necessarily recover results for P'^{∞} that are insensitive to the dynamics, since there is still competition between $\hat{k}_1$ and T_1-type processes, the latter being dependent on the rate of rotational reorientation. Of course, such conclusions will be altered if other types of processes begin to be important in T_1.

It should be noted that once the radical pair is formed with initial polarization given by Eq. (6.24), then the RPM of Sections II–IV can become effective, so that the total final polarization P^{∞}, when the radical pair separates never to reencounter, is given for radical A by the complete equation (2.15a).

C. Effect of Polarized Light

Adrian[41] has recently suggested that the initial triplet polarization can be sensitive to the direction of the polarized light relative to the applied dc field. This may be incorporated into the present approach by rewriting Eq. (6.4) as

$$\dot{\rho} = -i\mathscr{H}^{\times}\rho - \Gamma(\rho - \rho_{eq}) - (\hat{k}_1 + \hat{k}_2)\rho + \mathbf{k}_3(\Omega)\rho_s(t) \tag{6.39}$$

where the excited singlet distribution function $\rho_s(\Omega, t)$ obeys

$$\dot{\rho}_s = -\hat{k}_3\rho_s - \Gamma\rho_s. \tag{6.40a}$$

Also

$$\dot{\sigma}(t) = \hat{k}_3\rho(s) - (\hat{k}_1 + \hat{k}_2)\sigma. \tag{6.40b}$$

Here

$$\mathbf{k}_3(\Omega) = \hat{k}_3[w_{x'}|X'\rangle\langle X'| + w_{y'}|Y'\rangle\langle Y'| + w_{z'}|Z'\rangle\langle Z'|]; \tag{6.41}$$

cf. the right-hand side of Eq. (6.25). Thus $\hat{k}_3 = \mathrm{Tr}\mathbf{k}_3(\Omega)$ and we let

$$\int \rho_s(\Omega, t = 0)d\Omega = 1 \tag{6.42}$$

where $\rho_s(\Omega, t = 0)$ gives the initial polarization of the excited singlets due to the polarized light. One then finds that the right-hand sides of Eqs. (6.11) become $\rho_{eq}(0)\hat{k}_3/[s + \hat{k}_3]$ and $[\mathbf{k}_3(\Omega) - \hat{k}_3\rho_{eq}(0)]\rho_s(\Omega, 0)/[s + \Gamma + \hat{k}_3]$, respectively. It is easy to see that for an isotropic initial distribution, i.e., $\rho_s(\Omega, 0) = 1/8\pi^2$, in the limit $s \to 0$ the results using Eq. (6.25) are recovered.

[41] F. J. Adrian, *J. Chem. Phys.* **61**, 4875 (1974).

However, in general, the final solution will depend on the orientational distribution of $\rho_s(\Omega, 0)$. The solution may be obtained by the methods already described.

Adrian gives a perturbation-type analysis and finds that the CIDEP polarizations can vary by as much as 20% by changing the axis of light polarization.[41] Recently such effects appear to have been seen.[42]

VII. Signal Intensities and Time-Resolved Experiments

In this section we relate the polarizations, as discussed in the earlier sections, to the ESR and NMR intensities which are observed in an experiment.

A. CIDEP Intensities and Enhancements

The ESR intensity depends on the difference in populations of the $S_z = \frac{1}{2}$ and $S_z = -\frac{1}{2}$ levels which is the electron polarization [cf. Eq. (2.13b)]. For an equilibrium system the polarization P_{eq} is determined by the Boltzman distribution ($P_{eq} \simeq 1.4 \times 10^{-3}$ for a X-band experiment), and it is almost independent of the hyperfine state. The polarization of a radical created during a collision with another radical or at the formation stage of the radical will decay to the equilibrium value P_{eq} due to a T_1 process. Also the ESR signal depends upon the concentration of the radicals carrying the polarization, and these radicals may be destroyed due to chemical processes, and new radicals may form. Therefore a complete description of the kinetics of the system is necessary in order to interpret a time-dependent ESR signal.

1. *General Treatment*

For ease in the presentation we shall use kinetic equations of the type

$$dn_a(t)/dt = k_{0,a} - k_{1,a}n_a(t) - \sum_b k_2\mathscr{F}_{ab}n_a(t)n_b(t), \tag{7.1a}$$

$$dn_b(t)/dt = k_{0,b} - k_{1,b}n_b(t) - \sum_a k_2\mathscr{F}_{ab}n_a(t)n_b(t), \tag{7.1b}$$

although the method is applicable to any kinetic model. Here $n_a(t)$ and $n_b(t)$ represent the number density (or concentration) of radicals A and B in specific nuclear states. The zero-order (k_0) terms represent the formation of the radicals by a radical source, e.g., a light source or an electron beam. We assume that the radicals are created by a zero-order reaction only, which is probably a good approximation when the radicals are produced by photolytic or radiolytic dissociation of a precursor molecule which is present in a high concentration. If there is a production of radicals A by a reaction involving

[42] B. B. Adeleke, K. Y. Choo, and J. K. S. Wan, *J. Chem. Phys.* **62**, 3822 (1975).

other radicals then this production term may be included as well. The first-order reaction may be due to reactive collision with other radicals or molecules where for convenience it is assumed that the concentration of the latter is sufficiently large so that this concentration hardly changes. Also we assume that this first-order process does not produce any observable polarization. The second-order reaction is the spin-selective reaction, i.e., only radical pairs in singlet states can react. The rate constant is most conveniently written as $k_2\mathscr{F}_{ab}$, where $k_2 n_a(t)n_b(t)$ gives the frequency of collision of A and B in the specified nuclear states and $\mathscr{F}_{ab}$ gives the probability of reaction per collision (cf. Section III). k_2 depends only on the diffusion constant and the distance of closest approach [cf. Eq. (3.8)].

Although it is the spin-selective reaction that causes the RPM electron spin polarization, it is generally not possible to directly observe the reactivity of the radicals as a function of the radical nuclear states (actually the Q-values of the radical pairs) in ESR. Any anomalous population of the radical nuclear states arising from the spin-selective reaction will decay by nuclear spin-lattice relaxation to the equilibrium population, which in most ESR experiments may be taken to be equal populations. For a rigorous description of $n_a(t)$ and $n_b(t)$ one should then include the nuclear spin relaxation in Eqs. (7.1) (cf. Pedersen[12]). As the ESR intensity is proportional to $n_a(t)$ while an NMR signal is proportional to the difference $n_a(t)-n_{a'}(t)$ the different reactivity of the different nuclear states show up much more directly in NMR. The maximum enhancement found in NMR is of the order of 10^3 which corresponds to $[n_a(t)-n_{a'}(t)]/n_a(t) \simeq 10^{-2}$. It is therefore a good approximation in ESR to assume that $n_a(t)$ for all nuclear states are identical and equal to $n_A^{eq}(t)$ where $n_A^{eq}(t)$ is the average value of $n(t)$.

$$n_A^{eq}(t) = 1/x_A \sum_a n_a(t) \tag{7.2}$$

and x_A is the number of different nuclear levels of radical A.

If one neglects the nuclear spin relaxation, one can obtain rate equations for $n_A(t) = x_A n_A^{eq}(t)$ and $n_B(t) = x_B n_B^{eq}(t)$ (the total number of radicals A and B) summing Eqs. (7.1a) and (7.1b) over a and b, respectively (i.e., over all nuclear levels of radical A and B). The resulting rate equations are similar to normal rate equations:

$$dn_A(t)/dt = k_{0,A}(t) - k_{1,A}n_A(t) - k_2\mathscr{F}n_A(t)n_B(t) \tag{7.3a}$$

$$dn_B(t)/dt = k_{0,B}(t) - k_{1,B}n_B(t) - k_2\mathscr{F}n_A(t)n_B(t) \tag{7.3b}$$

where

$$k_{0,A} = \sum_a k_{0,a} \tag{7.4a}$$

and

$$\mathscr{F} = \sum_{a,b} \mathscr{F}_{ab}/(x_A x_B) \tag{7.4b}$$

but they explicitly include the effect of the spin selective reaction through $\mathscr{F}$. We have included a time-dependent k_0 for generality. Note that $k_{1,a} = k_{1,A}$ since we have assumed that the first-order process is not spin selective. In deriving rate equations for the intensity, we shall use a Bloch equation approach. The z-component of the magnetization of radical A in nuclear state a is then given by

$$M_z^a(t) = n_a(t)\,P_a(t) \tag{7.5}$$

where $P_a(t)$ is the electron polarization of radical A in nuclear state a. The rate of change of $M_z^a(t)$ due to the kinetics may be expressed in terms of the different, independent processes as

$$dM_z^a/dt = dM_z^a/dt]_{k_{0,a}} + dM_z^a/dt]_{k_1} + dM_z^a/dt]_{k_2}. \tag{7.6}$$

The first term in Eq. (7.6) may be explicitly written as

$$dM_z^a/dt]_{k_{0,a}} = P_a^\infty(I)(dn_a/dt)_{k_{0,a}} = P_a^\infty(I)k_{0,a} \tag{7.7a}$$

where $P_a^\infty(I)$ is the polarization at the formative stage of the radical. This polarization may be generated by the radical pair mechanism (cf. Sections III and IV) and/or the triplet mechanism (cf. Section VI). No distinction between these two mechanisms can be made purely on the ground that the polarization is an initial polarization. Instead it must be made on the different dependences of P_a^∞ upon the parameters D, Q, etc. If the initial polarization is generated by the RPM, and the radicals initially form a triplet state, then

$$P_a^\infty(I) = x_B^{-1} \sum_b P_{ab}^\infty(T) \tag{7.7b}$$

where the summation extends over all hyperfine levels of the other radical B. Note that if the radical A is formed by a reaction of another radical with a molecule, then any polarization (e.g., equilibrium polarization) of the latter radical may be transferred to radical A and this polarization would then be the initial polarization of A [$P_a^\infty(I)$]. The k_1 term can immediately be written as

$$dM_z^a/dt = P_a(t)\,dn/dt|_{k_1} = -k_1 M_z^a(t). \tag{7.7c}$$

The k_2 term, which invloves collision between two independently produced radicals a and b under the effect of an exchange interaction, is the most difficult to treat because it involves both polarization production (by spin-selective reaction of the radicals and RPM) and a polarization quenching of existing polarization (by Heisenberg spin exchange). The rate of collisions of A and B is simply given by $k_2 n_A(t)n_B(t)$ when the combined spin state of A and B is unspecified. The polarization produced during a reactive collision between two randomly distributed radicals is P_{ab}^∞ and the fraction that reacts is $\mathscr{F}_{ab}$ (note that $P_{ab}^\infty/\mathscr{F}_{ab}$ is independent of the reactivity; cf. Sections III and

IV). However, if the two radicals have polarization $P_a(t)$ and $P_b(t)$ when they first encounter, then we must examine the density matrix at that time.

A first encounter at time t between two radicals with polarizations $P_a(t)$ and $P_b(t)$ will lead to the diagonal matrix elements (in the doublet representation)

$$\rho_{a+,b-} = \tfrac{1}{4}[1-P_a(t)][1+P_b(t)] \tag{7.8a}$$

$$\rho_{a-,b+} = \tfrac{1}{4}[1+P_a(t)][1-P_b(t)] \tag{7.8b}$$

and the off-diagonal elements, e.g., $\rho_{a+,b-;a-,b+}$, equal to zero, i.e., no initial phase coherence between the states. The density matrix elements in the doublet representation may be converted to the $S, T_0, T_\pm$ representation by the equations given after Eqs. (2.15) and we get

$$\rho_{S,S}(t) = \rho_{T_0,T_0}(t) = \tfrac{1}{4}[1-P_a(t)\,P_b(t)], \tag{7.8c}$$

$$\rho_{S,T_0}(t) = \tfrac{1}{4}[P_b(t)-P_a(t)]. \tag{7.8d}$$

Equation (7.8c) shows that a random collision always yields equal S and T_0 character. Now usually $|P_a(t)|$, $|P_b(t)|$ are very small compared to unity (<0.1) so to a good approximation

$$\rho_{S,S}(t) = \rho_{T_0,T_0}(t) \simeq \tfrac{1}{4}, \tag{7.8e}$$

and k_2 simply refers to half the total number of collisions (the other half being the T_+ or T_- collisions which have no effect on the system). Equation (7.8d) shows that there is an initial nonzero $\rho_{S,T_0}(t)$ that is real. This polarization quantity is altered during the collision as described in Section IV, and the change is equal to $-\Delta P\cdot\rho_{S,T}(t)$. We can now summarize the k_2 contributions to dM_z^a/dt as

$$dM_z^a/dt|_{k_2} = \sum_b k_2\, n_a(t) n_b(t)[P_{ab}^\infty - \Delta P(P_a(t)-P_b(t))]. \tag{7.8f}$$

By adding the different contributions to the rate equation of $M_z^a(t)$, and neglecting the small hyperfine dependence of $n_a(t)$, one then obtains (cf. Pedersen.[12])

$$dM_z^a(t)/dt = -k_2\mathscr{F}\frac{\Delta P}{\mathscr{F}}[n_B(t)\,M_z^a(t)-n_A(t)\,M_z^B(t)]$$

$$+P_a^\infty(I)k_{0,A}(t)+k_2\mathscr{F}P_a^* n_A(t)n_B(t)-k_{1,A}M_z^a(t), \tag{7.9a}$$

where P_a^* is defined as

$$P_a^* = P_a^\infty/\mathscr{F} = \left(\sum_b P_{ab}^\infty X_B^{-1}\right)\Big/\mathscr{F}. \tag{7.9b}$$

The dependence of $\mathscr{F}_{ab}$ (R.I.) on the nuclear states is much weaker than that of P_{ab}^*, so to a good approximation

$$P_a^* \simeq \sum_b (P_{ab}^\infty/\mathscr{F}_{ab})/x_B = x_B^{-1}\sum_b P_{ab}^\infty(T)_{k=0}. \tag{7.9c}$$

Note that the reactivity of the system is only reflected through $\mathscr{F}$ [i.e., $n_A(t)$] since P_a^* is constant. This analysis shows that for a R.I. condition $P^\infty/\mathscr{F}$ is the important quantity. The Bloch equations appropriate for this system may be written as

$$dM_x^a(t)/dt = -T_2^{-1}M_x^a(t)+\Delta\omega M_y^a(t), \tag{7.10a}$$

$$dM_y^a(t)/dt = -\Delta\omega M_x^a(t)-T_2^{-1}M_y^a(t)-\omega_1 M_z^a(t), \tag{7.10b}$$

$$dM_z^a(t)/dt = \omega_1 M_y^a(t)-T_1^{-1}M_z^a(t)+n_A(t)T_1^{-1}P_{eq}+dM_z^a(t)/dt|_{eq.\,(7.9a)}. \tag{7.10c}$$

The magnetization of radical A, $\mathbf{M}^a$ is coupled to the magnetization of radical B, $\mathbf{M}^b$, by the ΔP term in Eq. (7.9b). However, in most experimental conditions one has $T_1\beta \ll 1$ (β^{-1} is the radical half-lifetime) and this assures a neglect of the ΔP term. In the original work[12] a special case with $\beta T_1 > 1$ and the ΔP term included was treated, but here we neglect this term.

Without the ΔP term in Eq. (7.8) one can write Eqs. (7.10) as

$$\dot{\mathbf{M}}(t) = \mathbf{L}\mathbf{M}(t)+\mathbf{F}(t) \tag{7.11}$$

where the time-independent matrix $\mathbf{L}$ is given by

$$\mathbf{L} = \begin{pmatrix} -T_2^{-1} & \Delta\omega & 0 \\ -\Delta\omega & -T_2^{-1} & \omega_1 \\ 0 & \omega_1 & -T_0^{-1} \end{pmatrix}. \tag{7.12}$$

T_0^{-1} is given by

$$T_0^{-1} = T_1^{-1}+k_1. \tag{7.13}$$

$\mathbf{F}(t)$ is given by

$$F(t) = \begin{pmatrix} 0 \\ 0 \\ f_a(t) \end{pmatrix} \tag{7.14a}$$

and

$$f_a(t) = P_a^\infty(I)k_{0,A}(t)+P_{eq}T_1^{-1}n_A(t)+k_2\mathscr{F}P_a^* n_A(t)n_B(t). \tag{7.14b}$$

By Laplace transformation of Eq. (7.11), we obtain

$$\mathbf{L}(s)\mathbf{M}(s) = \mathbf{M}(0)+\mathbf{F}(s) \tag{7.15}$$

where

$$\mathbf{L}(s) = -\mathbf{L}+s\mathbf{1} \tag{7.16}$$

and $\mathbf{M}(0)$ is the initial magnetization. The solution for $\mathbf{M}(s)$ can formally be written

$$\mathbf{M}(s) = \mathbf{L}(s)^{-1}[\mathbf{M}(0)+\mathbf{F}(s)]. \tag{7.17}$$

The solution is simply written for $\Delta\omega = 0$, i.e., one is observing the intensity at the center of the line.

$$M_y(t) = m_0 \cdot g_y(t) + f(t)^* g_y(t) + y_0 \cdot g_x'(t) \tag{7.18}$$

$$M_x(t) = m_0 \cdot g_x(t) + f(t)^* g_x(t) - y_0 \cdot g_y(t) \tag{7.19}$$

where m_0 and y_0 are the initial values of M_x and M_y, respectively, and

$$g_y(t) = -[\omega_1/(r_+ - r_-)][\exp(r_+ t) - \exp(r_- t)], \tag{7.20a}$$

$$g_x(t) = [1/(r_+ - r_-)][r_+ \exp(r_+ t) - r_- \exp(r_- t)] + [T_2^{-1}/(r_+ + r_-)][\exp(r_+ t) - \exp(r_- t)], \tag{7.20b}$$

and

$$r_\pm = -\tfrac{1}{2}(T_0^{-1} + T_2^{-1}) \pm [\tfrac{1}{4}(T_0^{-1} - T_2^{-1})^2 - \omega_1^2]^{1/2}. \tag{7.21}$$

$g_x'(t)$ is obtained by replacing T_2^{-1} by T_0^{-1} in Eq. (7.20b). $f(t)^* g(t)$ means the convolution of $f(t)$ with $g(t)$.

For the case $T_2 = T_0 = T_1$, which is assumed in the following examples, one finds (cf. ref. 12) that $g_y(t)$, $g_x(t)$, and $g_x'(t)$ are given by

$$g_y(t) = e^{-t/T_1} \sin \omega_1 t, \tag{7.22}$$

$$g_x(t) = g_x'(t) = e^{-t/T_1} \cos \omega_1 t. \tag{7.23}$$

2. *Slow Radical Decay*

We now assume that the lifetime of the radicals is much longer than the electron spin-lattice relaxation time T_1. We then have $T_0^{-1} = T_1^{-1}$ and we also make the simplifying assumption that $T_1 = T_2$ for simplicity of illustration.

The general form of the time-dependent intensity, i.e., $M_y(t)$, may be obtained from Eqs. (7.18), (7.22), and (7.23) as

$$M_y(t) = m_0 \cdot e^{-t/T_1} \sin \omega_1 \tau + y_0 \cdot e^{-t/T_1} \sin \omega_1 t + \int_0^t e^{-\tau/T_1} \sin(\omega_1 \tau) f(t-\tau)\, d\tau. \tag{7.24}$$

One sees from Eq. (7.14b) that $f(t)$ varies essentially as $n(t)$ which, according to the assumption, is much slower than $e^{-\tau/T_1}$ and Eq. (7.24) may therefore be approximated by

$$M_y(t) = m_0 \cdot e^{-t/T_1} \sin \omega_1 t + y_0 \cdot e^{-t/T_1} \cos \omega_1 t + f(t) \cdot e^{-t/T_1} [\omega_1 e^{t/T_1} - \omega_1 \cos \omega_1 t - T_1^{-1} \sin \omega_1 t]/(T_1^{-1} + \omega_1^2). \tag{7.25}$$

One observes that any initial value of M_y or M_z is damped out during a time period of the order of T_1. One also observes that $M_y(t)$ changes from its initial value y_0 to approximately $f(0)$ [neglecting the constant factor $\omega_1 T_1^2/(1+T_1^2\omega_1^2)$] during a time period of the order of T_1 after which the time dependence follows $f(t)$. The effect of the sine and cosine terms is to give rise to wiggles damping out in time. Note that these wiggles are only significant for $t \leqslant T_1$ and may therefore not be observed. For weak observing power, i.e., $\omega_1 T_1 \ll 1$ one observes no wiggles at all since $\sin(\omega_1 t) \simeq \omega_1 t$ and $\cos(\omega_1 t) \simeq 1$. The effect of increasing the power, i.e., increasing ω_1, is therefore for $t > T_1$ just to change the intensity as given by the factor $\omega_1 T_1^2 (1+T_1^2\omega_1^2)^{-1}$ in Eq. (7.25).

There are essentially two types of time-resolved experiments: (1) the steady state experiment where, e.g., a constant light source is applied in a time period sufficiently long that a steady state is reached. The light is then turned off (as fast as possible) and is not turned on again before all radicals have disappeared. The intensity is recorded both in the light period and in the dark period. (2) In a pulse experiment the light is applied for a short time (usually shorter than T_1 sec, e.g., by using a pulsed laser) and the intensity is recorded from the moment the light pulse starts. We divide the following discussion to distinguish between these two types of experiments.

a. *Steady State Experiments.* In a steady state experiment one has $m_0 = y_0 = 0$ in the light period, and one can easily prove that $m_0 = y_0/\omega_1 T_1$[38] in the dark period when it is assumed that $\omega_1 T_1 \ll 1$. It is now useful to rewrite Eq. (7.25) in the form

$$M_y(t) \simeq M_y^0(1+t/T_1)\exp(-t/T_1) + f(t)[1-(1+t/T_1)\exp(-t/T_1)] \tag{7.26}$$

where we have omitted common constant factors and we have used $\omega_1 T_1 \ll 1$. M_y^0 is equal to zero and the steady state value in the light and dark periods, respectively. The light and dark periods are treated separately and $t = 0$ corresponds to the time when the light either goes on or off. It is also useful to rewrite $f(t)$ [Eq. (7.14b)] in the form

$$f(t) \simeq V(l,t) + [n(t)/n_0][1 + Vn(t)/n_0] \tag{7.27}$$

where we have omitted the constant factor $n_0 P_{eq} T_1^{-1}$ and where n_0 is equal to the steady state value of $n(t)$. Also for simplicity we have assumed $n_A(t) = n_B(t) = n(t)$.[12] The enhancement V due to the spin-selective recombination process is given by

$$V = P^\infty T_1 k_2 \mathscr{F} n_0 / P_{eq}. \tag{7.28}$$

The enhancement $V(l,t)$ due to initial polarization is given by

$$V(l,t) = P^\infty(t) T_1 k_0(t) / P_{eq} n_0.$$

In the following we make the simplifying assumption that $k_0(t)$ can be represented by a series of square waves, i.e., the light goes from completely off to completely on and vice versa during a time shorter than T_1.

To obtain the time dependence of the intensity for a specific case one just needs to solve the kinetic equations (7.3). We illustrate this by a few examples.

Example 1. Initial Polarization Only. First-Order Reaction. By solving the appropriate kinetic equations and substituting the result into Eq. (7.27) we immediately get

$$f(t) = \begin{cases} V(I) + [1 - \exp(-k_1 t)] & \text{light period} \quad (7.30a) \\ \exp(-k_1 t) & \text{dark period} \quad (7.30b) \end{cases}$$

$$V(I) = P^{\infty}(I) T_1 k_1 / P_{eq} \quad (7.31)$$

and $M_y^0 = 1 + V(I)$ for the dark period. By substituting $f(t)$ into Eq. (7.26)

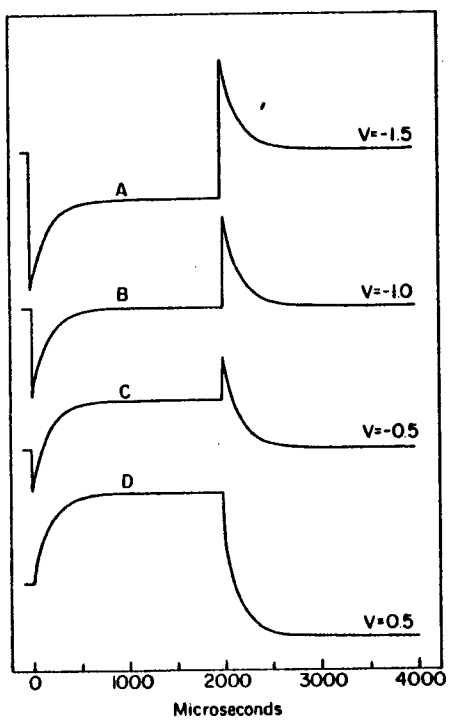


FIG. 11. Intensity versus time for initial polarization case (steady state experiment). The radical producing source, e.g., a light source, is assumed to have a constant power and to be turned on instantly at time zero and off instantly at 2000 μsec. Each curve corresponds to a different value of the enhancement V as indicated on the figure. Other parameters used are $T_1 = 2$ μsec, and $k_1^{-1} = 120$ μsec for all curves. [By permission from Pedersen.[12]]

one then obtains the complete time dependence. One observes that the intensity in the light period goes from zero to $V(I)$ during a time period of order T_1 and then decays with rate constant k_1 to the steady state value $1 + V(I)$, which of course is also proportional to the signal for the spectral line recorded during continuous light illumination. For the line to appear in emission, one requires $V(I) < -1$. In the dark period the intensity goes from $1 + V(I)$ to 1 during a time period of order T_1 and decays with the rate constant k_1 to zero. Figure 11 displays the full time dependence for several values of $V(I)$. In principle, one should be able to obtain $V(I)$, k_1, and T_1 from such an experiment and $P^{\infty}(I)$ could then be calculated, but the T_1 is usually difficult to obtain due to the time resolution of the spectrometer (see below).

Example 2. Only Recombination Polarization. Second-Order Reaction. With the appropriate solutions of the kinetic equation one obtains

$$f(t) = \begin{cases} \tanh(\beta t)[1 + V \tanh(\beta t)] & \text{light period} \quad (7.32a) \\ (1+\beta t)^{-1}[1 + V(1+\beta t)^{-1}] & \text{dark period} \quad (7.32b) \end{cases}$$

where the second-order decay constant β equals

$$\beta = k_2 \mathcal{F} n_0 \quad (7.33)$$

and the enhancement V then becomes

$$V = P^{\infty} T_1 \beta / P_{eq}. \quad (7.34)$$

The complete time dependence is then given by Eqs. (7.32) and Eq. (7.26) and is displayed in Fig. 12.

One observes a marked difference in the time dependence between these two examples which enables one to distinguish between these two cases. Other kinetic systems may be treated similarly, e.g., one could have both initial and recombination polarization, which, as seen from Eq. (7.27), can be obtained as a superposition of a pure initial polarization case and a pure recombination polarization case with the same kinetics (cf. Pedersen *et al.*[38]).

b. *Pulse Experiments.* If the duration of the pulse is much longer than T_1 then Eq. (7.26) with $M_y^0 = 0$ and Eq. (7.27) are again applicable. If the duration of the pulse is much shorter than T_1 then one just gets

$$M_y(t) = (t/T_1) \exp(-t/T_1) P^{\infty}(I)/P_{eq} + n(t)/n_0 [1 - (1 + t/T_1) \exp(-t/T_1)] \times [1 + V n(t)/n_0] \quad (7.35)$$

where V is again given by Eqs. (7.28) and (7.29), but where n_0 is now the initial value of $n(t)$ just after the end of the pulse. For a second-order decay V is given by Eq. (7.34).

c. *Spectrometer Response.* A word of caution should be given in applying

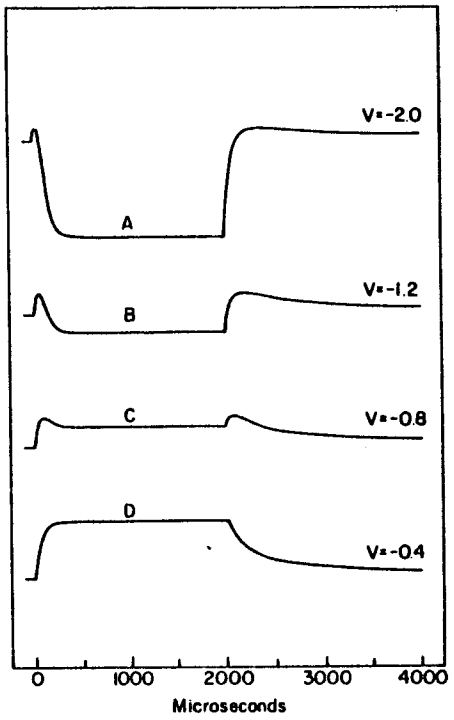


FIG. 12. Intensity versus time for recombination polarization case (steady state experiment). The radical producing source, e.g., a light source, is assumed to have a constant power and to be turned on instantly at time zero and off instantly at 2000 μsec. Each curve corresponds to a different value of the enhancement V as indicated on the figure. Other parameters used are $T_1 = 2$ μsec and $\beta = 120$ μsec for all curves. [By permission from Pedersen.[12]]

the above equation to an experiment. In the above discussion nothing has been said about the spectrometer response. If one defines a response function $\mathcal{G}(t)$ as the spectrometer's response to a δ pulse (in time) then a general spectrometer input $M_y(t)$ will result in a spectrometer output $O(t)$ given by

$$O(t) = \int_{-\infty}^{t} \mathcal{G}(t-\tau)\, M_y(\tau)\, d\tau. \tag{7.36}$$

If one characterizes the response function by a response time τ_g, then this is normally of the order of 30–150 μsec using 100 kHz modulation, but it can be decreased by using 2 MHz modulation to about 2–3 μsec. More details about response functions and how this influences the above equations for $M_y(t)$ may be found in Pedersen *et al.*[38] A review of the experimental methods has been given by Atkins and McLauchlan.[43]

[43] P. W. Atkins and K. A. McLauchlan, Lepley and Closs.[1]

3. *Fast Chemical Decay*

When the half-life of the radicals becomes comparable to or smaller than T_1, then Eq. (7.25) and the above equations for a slow radical decay no longer apply. If one can neglect Heisenberg spin exchange, i.e., the ΔP term in Eq. (7.9a), then Eq. (7.24) is applicable. But, if the ΔP must be included, then one must solve coupled equations. Also effects due to $T_1 \neq T_2$, field inhomogeneity, and the application of high observing power become important when the radical lifetime is comparable to T_1 and observations for $t \lesssim T_1$ are needed. This is discussed in detail in Pedersen.[12]

B. CIDNP Intensities and Enhancements

We now relate the $\mathcal{F}$'s calculated in Sections III and IV with the intensities as observed in a CIDNP experiment. We wish to point out that within the usual assumption of negligible cross-relaxation, one can easily obtain exact relations for the time-dependent intensities. Such relations are important both for obtaining rate constants as well as determining the $\mathcal{F}$'s by a CIDNP experiment. The approach is similar to that already discussed. Here we assume for simplicity that the intensity is described by the z-component of the magnetization, as is indeed the case for $t > T_1$. The proper modifications needed if one is interested in times smaller than or of the order of T_1 are very similar to those discussed for CIDEP.

The following simple reaction scheme is considered for illustration.

$$S \rightarrow \overline{R_a^\bullet + R_b^\bullet} \rightarrow R_{ab}$$
$$\searrow$$
$$R_a^\bullet + R_b^\bullet.$$

The precursor S decomposes into a radical pair $\overline{R_a^\bullet + R_b^\bullet}$ where the bar indicates that the radicals are initially close together. This initialization process is assumed to be a first-order or pseudo-first-order reaction with reaction constant k_0'. $R_a^\bullet$ means radical A in a specific nuclear state a. The two radicals, initially together, may diffuse apart into $R_a^\bullet + R_b^\bullet$, never to meet again, in which case the radicals end up in scavenging products or they may, after a diffusive excursion, recombine to give a recombination product R_{ab}. In the following $S(t)$ and $R(t)$ are the total concentration at time t, respectively, of the precursor and of the recombination products, irrespective of the nuclear states, while $R_{ab}(t)$ is the concentration at time t of a recombination product in a specific nuclear state specified by the subscript.

If we assume that the recombination product R is different from precursor S, then the rate equation for S yields

$$S(t) = S(0)\exp(-k_0' t). \tag{7.37}$$

The rate of formation of a specific radical pair $\overline{R_a^\bullet + R_b^\bullet}$ is $k_0' X_s^{-1} S(t)$, where it is assumed that all nuclear states of the precursor are equally populated. X_s is the nuclear degeneracy of S. The fraction of radical pairs $R_a^\bullet + R_b^\bullet$ that recombine to give recombination product R_{ab} is $\mathscr{F}_{ab}$ (where the subscripts serve to define the Q-value when the g-values and hyperfine splittings are known). The rate equation for $R_{ab}(t)$ is therefore

$$d/dt\ R_{ab}(t) = k_0' X_s^{-1} \mathscr{F}_{ab} S(t) - T_1^{-1}[R_{ab}(t) - R_{ab}^{eq}(t)] \qquad (7.38a)$$

where the last term gives the spin-lattice relaxation. A single averaged relaxation time T_1 is assumed and cross-relaxation between different nuclear states is neglected. This may be a rather crude approximation and is assumed here for ease in the presentation. $R_{ab}^{eq}(t)$ is defined as

$$R_{ab}^{eq}(t) = p_{ab}^{eq} R(t) \qquad (7.38b)$$

where p_{ab}^{eq} is the Boltzmann population of product state ab. The rate equation for $R(t)$ is obtained by summing Eq. (7.38a) over all states a and b

$$dR(t)/dt = k_0' X_s^{-1} \mathscr{F} S(t) \qquad (7.39a)$$

where

$$\mathscr{F} \equiv \sum_{a,b} \mathscr{F}_{ab}. \qquad (7.39b)$$

Equations (7.39a) and (7.37) give

$$R(t) = X_s^{-1} \mathscr{F} S(0)(1 - e^{-k_0' t}). \qquad (7.39c)$$

[Note that when $S(t) \approx S(0)$ over the interval of the experiment, we have $k_{0,a}$ of Eq. (7.1) equal to $k_0' X_A^{-1} S(0)$ for this case. Also note that $X_s = X_A X_B$.] Equation (7.38a) may be solved, using Eqs. (7.37), (7.38b), and (7.39c), to give

$$R_{ab}(t) = p_{ab}^{eq} X_s^{-1} \mathscr{F} S(0)(1 - e^{-t/T_1}) + X_s^{-1} S(0) \mathscr{F} (k_0 \mathscr{F}_{ab}/\mathscr{F} - T_1^{-1} p_{ab}^{eq})(T_1^{-1} - k_0)^{-1} (e^{-k_0' t} - e^{-t/T_1}) \quad \text{for} \quad T_1^{-1} \neq k_0' \qquad (7.40a)$$

and

$$R_{ab}(t) = p_{ab}^{eq} X_s^{-1} \mathscr{F} S(0)(1 - e^{-t/T_1}) + X_s^{-1} S(0) \mathscr{F} (k_0 \mathscr{F}_{ab}/\mathscr{F} - T_1^{-1} p_{ab}^{eq}) \cdot t \quad \text{for} \quad T_1^{-1} = k_0'. \qquad (7.40b)$$

Equations (7.40) give the exact time dependence of $R_{ab}(t)$ without any simplifying assumption of steady state and/or constant precursor concentrations.

Use of these equations permits a clearer interpretation of the experimental results. However, we shall only consider as a specific example a slow reaction.

Slow reaction: i.e., $T_1^{-1} \gg k_0'$ then $(T_1^{-1} - k_0')^{-1} \simeq T_1$ and Eq. (7.40a) is approximated by

$$R_{ab}(t) = S(0) X_s^{-1} \mathscr{F} p_{ab}^{eq}(1 - e^{-k_0' t}) + S(0) X_s^{-1} \mathscr{F}_{ab} k_0 T_1 (e^{-k_0' t} - e^{-t/T_1}). \qquad (7.41)$$

Consider an NMR transition ab → a + 1b, then the intensity of this line is proportional to

$$I_{ab,a+1b}(t) = R_{ab}(t) - R_{a+1b}(t) = S(0) X_s^{-1} \mathscr{F}(1 - e^{-k_0' t})(p_{ab}^{eq} - p_{a+1b}^{eq}) + S(0) X_s^{-1} k_0' T_1 (e^{-k_0' t} - e^{-t/T_1})(\mathscr{F}_{ab} - \mathscr{F}_{a+1b}) \qquad (7.42)$$

which has exactly the same form as Eq. (7.41).

If one had used the complete Eqs. (7.40) a very similar result would have been obtained with the obvious changes in it of

$$\mathscr{F}_{ab} \to \mathscr{F}_{ab} - \mathscr{F}_{a+1b} = (\mathscr{F}_{ab} - \mathscr{F}_0) - (\mathscr{F}_{a+1b} - \mathscr{F}_0) \qquad (7.43a)$$

$$p_{ab}^{eq} \to p_{ab}^{eq} - p_{a+1b}^{eq}. \qquad (7.43b)$$

Equation (7.42) can be rewritten as

$$I_{ab,a+1b} = S(0) X_s^{-1} (\mathscr{F}_{ab} - \mathscr{F}_{a+1b}) k_0' T_1 (1 - e^{-t/T_1}) + S(0) X_s^{-1} (\mathscr{F}_{ab} - \mathscr{F}_{a+1b}) k_0' T_1 \left[\frac{p_{ab}^{eq} - p_{a+1b}^{eq}}{\mathscr{F}_{ab} - \mathscr{F}_{a+1b}} \frac{\mathscr{F}}{k_0' T_1} - 1 \right] (1 - e^{-k_0' t}) \qquad (7.44)$$

The maximum intensity $I_{ab,a+1b}(\max)$ is seen to occur for $t \gtrsim T_1$ and is equal to

$$I_{ab,a+1b}(\max) = S(0) X_s^{-1} (\mathscr{F}_{ab} - \mathscr{F}_{a+1b}) k_0 T_1. \qquad (7.45a)$$

Thus Eq. (7.44) may be written as

$$I_{ab,a+1b}(t) = I_{ab,a+1b}(\max) \times \left\{ (1 - e^{-t/T_1}) + \left[\frac{p_{ab}^{eq} - p_{a+1b}^{eq}}{\mathscr{F}_{ab} - \mathscr{F}_{a+1b}} \frac{\mathscr{F}}{k_0 T_1} - 1 \right] (1 - e^{-k_0' t}) \right\}. \qquad (7.45b)$$

The intensity goes to a maximum value during a time of the order of T_1 and then decays exponentially with time constant k_0' to a limiting value $I_{ab,a+1b}(\infty)$. This behavior is commonly seen,[44] but does not appear to have been given a proper expression such as that of Eq. (7.45b). Also

$$I_{ab,a+1b}(\infty) = S(0) X_s^{-1} (p_{ab}^{eq} - p_{a+1b}^{eq}) \mathscr{F} \qquad (7.46)$$

[44] J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch. A* 22, 1551 (1967).

which is seen to be just the equilibrium intensity of the product when the reaction has gone to completion.

The intensity enhancement, i.e., the actual intensity at time t as given by Eq. (7.45b) divided by the intensity the product at time t would have had if the nuclear state population was given by a Boltzmann distribution, is easily calculated by Eq. (7.45b). However, such a quantity is not always experimentally convenient to obtain. Instead in cases where one can measure $I(\infty)$ of Eq. (7.46) (e.g., when the product disappears at a slower rate than it is formed, as assumed in the above example), one may define a useful experimental enhancement V^{exp} as

$$V^{exp}_{ab,a+1b} = I_{ab,a+1b}(max)/I_{ab,a+1b}(\infty) \tag{7.47a}$$

which, by use of Eqs. (7.45a) and (7.46), becomes

$$V^{exp}_{ab,a+1b} = (\mathscr{F}_{ab}-\mathscr{F}_{a+1b})k_0'T_1/(p^{eq}_{ab}-p^{eq}_{a+1b})\mathscr{F}. \tag{7.47b}$$

The maximum real enhancement $V^{max}_{ab,a+1b}$ that occurs for $t \simeq T_1$ is easily seen from Eq. (7.44) to be

$$V^{max}_{ab,a+1b} = 1 + (\mathscr{F}_{ab}-\mathscr{F}_{a+1b})/\mathscr{F}(p^{eq}_{ab}-p^{eq}_{a+1b}) \tag{7.47c}$$

where the 1 is usually negligible.

If the nuclear states ab and a+1b consist of independent states a and b then the intensity and the enhancement of the line a → a+1 is obtained in the usual manner by summing Eqs. (7.45), (7.46), and (7.47) over states b.

The experimental enhancement (or the real enhancement) for a specific precursor (S, T_0, or R.I.) may be obtained from Eq. (7.47b) and the earlier expressions for $\mathscr{F}$. The result for a triplet precursor shows a very weak dependence on Λ, i.e., of the reactivity of the radicals. For a singlet we have that the enhancement [which has a sign opposite to that for the triplet (and R.I.) case] goes to zero for $\Lambda \to 1$ (high reactivity of the radicals). But note that this need not be true if the radicals are created with a large kinetic energy so that $r_0 \neq d$ (cf. Section III), in which case however the enhancement will be small. The enhancement is maximum for $\Lambda = 0$, but then all radicals end up in scavenging products and no signal due to a recombination product is observed. The optimal experimental condition will then be for $\Lambda \simeq \frac{1}{2}$.

For a R.I. (or F) precursor (note that the initialization step, i.e., the first encounter, is assumed to be described by a pseudo-first-order reaction) the enhancement is maximum for $\Lambda = 1$ and goes to zero as Λ goes to zero.

Results similar to those given here may be obtained in a similar manner for other reaction schemes, e.g., for scavenging products, or for identical precursor and recombination products. Modifications needed for $t < T_1$ may also be incorporated as noted. Inclusion of cross-relaxation would, however, require the solution of more complex matrix equations.

Appendix: Glossary of Symbols

(We include, in brackets, the equation in the text in which the symbol first appears.)

a, b	refer to radicals A and B of radical pair
$A(\mathbf{r}-\mathbf{R})$	probability that a molecule jumps to position r from position R in a single step [5.6]
$A^{2,m}$	spin operators for zero-field splitting term [6.14]
$\mathscr{A}$	the complex matrix defined by Eqs. (6.19) and (6.11b)
B_0	the dc magnetic field intensity [2.3]
B_L	the rotational diffusion model parameter [6.16]
C	vector of expansion coefficients of $\chi(s')$ [6.19]
$d = r_0$	distance of closest approach of the radical pair (i.e., contact distance) [2.19]
d	vector of expansion coefficients of $\chi(t = 0)$ [6.19]
D	zero-field splitting parameter [6.14]
$D = D_a + D_b$	diffusion coefficient for relative motion of radical pair [2.1]
$D\Gamma_r, D\Gamma_r, D\hat{\Gamma}_r$	diffusion operator for relative diffusion of radical pair [2.1, 4.3]
$\mathscr{D}^L_{KM}(\Omega)$	generalized spherical harmonics (Wigner rotation matrices) [6.14]
eZ_i	charge on ith molecule [4.14]
E	zero-field splitting parameter [6.14]
$f_\ell(ur)$	modified spherical Bessel function including reflecting wall boundary condition [5.1, 5.5]
$f^*, f^*(r_i), \hat{f}^*$	Debye–Hückel corrections to bimolecular rate constant [4.16, 4.21, 4.32]
$F(r)r = \hat{F}(r)$	dimensionless magnitude of force of interaction between radical pair which can be spin-dependent [4.2, 4.4]
$\mathscr{F}, \mathscr{F}(N)$	probability of reaction for the radical pair per collision [2.17c, 4.42]
$\mathscr{F}_0$	the value of $\mathscr{F}$ calculated for $Q = 0$ [3.1]
$\mathscr{F}^*$	probability of reaction of triplets per collision for unit reactivity of singlets [3.2]
$\mathscr{F}_{ab}$	the value of $\mathscr{F}$ with a and b labeling the specific nuclear states of radicals A and B [7.1]
g_a, g_b	g-factors of radicals A and B [2.3]
$g(r)$	equilibrium pair-correlation function [4.24]
$\mathscr{G}(t)$	spectrometer response function [7.36]
H, h	functional forms for $\Delta P(d_i)$ [4.49, 4.50]
$\mathscr{H}^\times(\mathbf{r}_i)$	Liouville operator for the radical pair, associated with the spin Hamiltonian $\mathscr{H}(\mathbf{r}_i)$ [2.1–2.4]
$I_{ab,a+1b}(t)$	intensity factor for NMR transition between states a, b and a+1, b [7.42]
$\mathbf{I}_j$	nuclear spin operator of jth nucleus [2.3]
$j_\ell(ur)$	spherical Bessel function of first kind [5.2a, 5.3]
$J(\mathbf{r}_a, \mathbf{r}_b), J(r)$	exchange interaction between radical pair [2.3]
$J_0 \equiv J(r = d)$	
$J_0(max)$	the value of J_0 that gives the maximum value of $P^\infty/\mathscr{F}$ [3.17']
k	first-order rate constant for irreversible disappearance of singlet radical pairs when in contact [2.37]
$k_{0,a}, k_{0,b}, k_{0,A}, k_{0,B}$	zero-order rate of production of radicals (e.g., due to a light beam) [7.1, 7.3]
k_0'	(pseudo-) first-order rate constant for initial formation of radical pair from precursor [7.37]

$k_{1a}, k_{1b}, k_{1A}, k_{1B}$	(pseudo-) first-order rate constant for decay of radical pair [7.1, 7.3]
$k_2(r_1), k_2(d)$	one-half the second-order rate constant for new bimolecular collisions at separation r_1 or d [4.18, 4.22]
k_f	experimentally observed bimolecular rate constant [3.8]
k_1, k_2, k	(pseudo)-first-order rate constants for decay of initial triplets: k_1—into radical pairs, k_2—into other products, $k = k_1 + k_2$ [6.3, 6.4, 6.8]
k_3, k_3	first-order rate constant for formation of triplet from excited singlet [6.39, 6.40]
K	equilibrium constant between radical pairs and separated radicals [4.34]
$\mathscr{K}_r$	spin-dependent operator for reaction rate constants [2.1]
m_0, y_0	initial values of $M_x(t)$, $M_y(t)$ [7.19]
$M_x^a, M_y^a, M_z^a, \mathbf{M}$	the components of magnetization for the a radicals expressed in the laboratory frame, and the magnetization vector [7.5, 7.10, 7.11]
$n_a(t), n_b(t), n_i(t)$	number density of radicals A and B and of ith type of particle [4.15, 4.44]
n_0	the steady-state value of $n(t)$ [7.27]
$O(t)$	spectrometer output [7.36]
$\rho(r)$	classical distribution function for relative motion of the radical pair [4.1]
p_{ab}^{eq}	Boltzmann factor for diamagnetic product state ab [7.38b]
$P_a(t), P_a^\infty$ (or P^∞)	polarization of radical A at time t and at infinity [2.13b, 2.16b]
$P_a^\infty(r_1), P_a^\infty(r_1)$	P_a^∞ generated from an initial separation for the radical pair of r_1 [4.44], or transferred according to Eq. (4.46)
$P_a^\infty(N)$	the polarization of radical A for separated particles at $t \to \infty$ [4.40]
$P_a^\bullet \equiv P_a/\mathscr{F}$	[7.9]
P_{eq}	equilibrium polarization for ESR [7.10]
$\Delta P(r_1), \Delta P(r_4)$	the fractional change in the polarization from that which exists at the onset of the collision [4.44, 4.49]
$\mathscr{P}(t) \equiv 1 - \mathscr{F}(t)$	probability a radical pair has not reacted by time t [2.13a]
$\mathscr{P} \equiv 1 - \mathscr{F}$; $\mathscr{P}(N)$	probability a radical pair does not react per collision [2.16a, 4.41]
Q	half the difference in ESR resonant frequencies of the two interacting radicals [2.30]
$r_0 \equiv d$	distance of closest approach of the radical pair [2.19]
$r_{ex} = \lambda^{-1} 5 \ln 10$	[2.41]
r_1	separation of radical pair at the initiation of a collision [3.10]
r_M	separation distance such that $J(r > r_M)$ and $U(r > r_M)$ are zero [2.27]
r_N	position of outer absorbing wall [2.21]
$\Delta r, f\Delta r$	radial increments for finite differences [2.12, 2.27]
Δr_J	range of $J(r)$ for contact exchange [3.19]
Δr_k	range of rate constant k [2.37]
R	isotropic rotational diffusion coefficient [6.16]
$R(t), R_{ab}(t), R_{ab}^{eq}(t)$	the time-dependent concentration of recombination products, independent of nuclear spin states [$R(t)$] and for the ab-th nuclear spin state with $R_{ab}^{eq}(t)$ the equilibrium value of the latter [7.38, 7.39]
s	Laplace transform independent variable (inverse time) [2.10]
S	singlet state [2.15]
$S(t)$	time-dependent concentration of (diamagnetic) precursor to radical pair [7.37]
$\mathbf{S}_a, \mathbf{S}_b$	electron-spin operators for radicals A and B [2.3]
t	time [2.1]
t_r	reencounter probability for two particles initially separated by r_1 [3.10]
T_0	triplet, $M = 0$ state [2.15]

$T_\pm$	triplet, $M = \pm 1$ states [6.1]
T_1	longitudinal spin-relaxation time [3.30, 3.31]
T_2	transverse spin-relaxation time [3.30]
$\mathbf{T}(r)$	Oseen's tensor [4.28]
u	relative velocity between radicals A and B [5.17]
$U(r)$	potential energy of interaction between the radical pair, which can be spin-dependent [e.g., $U_{SS}(r)$ is potential for singlet radical pairs] [4.1]
$V(i)$	radial weighting factor for r_ith position for finite differences [2.23]
$V(l, t)$	the ESR enhancement due to the spin-selective recombination process [7.27]
$V_{ab,a+1b}^{exp}$	the experimental enhancement for the NMR transition between states ab and a + 1b [7.47]
$w_{x'}, w_{y'}, w_{z'}$	preferential probabilities of populating the $T_{x'}, T_{y'}, T_{z'}$ states [6.25]
$\mathbf{W}, \mathbf{W}'$	finite difference transition matrix for diffusion with elements $W_{i,j}$ [2.18]
$x = r/d - 1$	dimensionless radial distance [2.42]
x_A, x_B	the number of different nuclear levels of radicals A and B [7.2]
X_a	nuclear degeneracy of the diamagnetic precursor [7.38a]
$y_\ell(ur)$	spherical Bessel function of second kind [5.2b, 5.5]
$Y_\ell^m(\Omega)$	spherical harmonic [5.3]
$\beta \equiv (k_0 \mathscr{F} k_2)^{1/2}$	experimentally observed second-order decay constant [7.33]
β_e	Bohr magneton [2.3]
β	friction coefficient [5.17]
δ	an exponential correction factor [4.19]
ε	dielectric constant of solvent [4.15]
$\varepsilon, \varepsilon', \varepsilon''$	exponentials on Qd^2/D [3.14] and λd [3.16]
η	solvent viscosity [4.29]
κ	Debye's reciprocal thickness of the ionic layer [4.15]
$\mathbf{K}'$	finite difference matrix of the elements of $\mathscr{K}_r$ [2.31]
λ	exponential decay constant in r for $J(r)$ [2.41]
Λ	fractional probability of reaction (for $Q = 0$) of singlets for the whole reaction. The "reactivity" [3.1]
μ	reduced mass of radical pair
$\rho(\mathbf{r}_1, t), \rho(r, t)$	spin-density matrix for radical pair [2.1]
$\hat{\rho}(r, t) \equiv r\rho(r, t)$	[2.11]
$\rho_0(r) \equiv \rho(r, 0)$	[2.10]
ρ_{eq}	equilibrium spin-density matrix [6.4]
$\bar{\rho}(t)$	space-average of $\rho(\mathbf{r}_1, t)$ [2.13c]
$\sigma = sd^2/D$	dimensionless Laplace transform independent variable [2.43]
$\sigma(t)$	the trace of $\rho(t)$ for initial triplets [6.5]
$\tau = tD/d^2$	dimensionless time variable [2.42]
τ	mean time between molecular jumps [5.6]
$\tau_1, \tau_1(\lambda)$	lifetime for the encounter pair [3.6, 3.15]
$\tau_R = (6R)^{-1}$	[6.31]
$\Phi(x, \tau)$	dimensionless form of $\rho(r, t)$ [2.42]
χ	a correction factor, cf. Eq. (3.11)
χ	the deviation of ρ from ρ_{eq} [6.7]
ω_0	Larmour frequency [6.14]
$\omega_1 \equiv \gamma_e B_1$	the microwave field strength [7.10]
$\Delta\omega \equiv \omega - \omega_0$	with ω the applied microwave frequency [7.10]

Ω	finite-difference matrix of the elements of $\mathscr{H}^{\times}(\mathbf{r}_i)$ [2.31]
EFA	model with exchange forces absent in the diffusion equation
EFP	model with exchange forces present in the diffusion equation
RDM	relative diffusion model, an EFP model for which radical pairs are not permanently bound
RI	random initial case [3.4]
RPM	radical pair mechanism
SLE	stochastic Liouville equation [2.1, 6.4]

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