# Chemically induced dynamic spin polarization in two dimensional systems: Theoretical predictions

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Theoretical predictions for chemically induced dynamic spin polarization [CIDN(E)P] and Heisenberg spin exchange in two dimensional fluid systems are developed. An idealized model, which yields simple limiting results is first discussed in order to illustrate the importance of the geometrical aspects of this problem upon the CIDN(E)P observables. Pedersen-Freed theory, which employs numerical solutions of the stochastic-Liouville equation is then applied. This approach is appropriately modified in its use and analysis in order to fully exhibit the details of two dimensional kinetic and polarization processes. Specifically, the Laplace transformed results are calculated and related to the finite time results (rather than the  $t \rightarrow \infty$  asymptotes) due to logarithmic divergences in time which characterize two dimensional processes. Approximate empirical formulas are developed to describe our exact numerical results and they illustrate the profound effects of a change of dimensionality on the CIDN(E)P observables. These results are related to experimental observables by considering the role of processes which limit the time scale for the polarization (e.g., radical scavenging and  $T_1$ ) and by a consideration of the role of two dimensional bimolecular encounter theory on random initial encounters. Other aspects of two dimensional effects (e.g., time-dependent diffusion coefficients and concentration effects) are briefly noted.

### I. INTRODUCTION

Chemically induced dynamic spin polarization can be described as the non-Boltzmann population of nuclear and electronic spin states of radicals and their products resulting from chemical reactions carried out in magnetic fields. Experimentally, this method is a useful tool in the elucidation of organic reaction mechanisms and other reaction processes where radicals are involved.<sup>1</sup> The theory of chemically induced dynamic nuclear (and electronic) polarization [CIDN(E)P] in threedimensional (i.e., normal) solutions has now been well explained, especially by the use of numerical solutions by the stochastic-Liouville approach.<sup>2</sup> The CIDNP problem in the absence of spin exchange [i.e., J(r)=0]also can be treated analytically, <sup>3a</sup> in terms of a model which allows a mathematical separation of the diffusive encounter phenomenon and the time evolution of the guantum spin states. When spin exchange with finite spatial extent is included, as is required in the CIDEP problem, typically numerical solutions of the stochastic-Liouville equation (SLE) are needed for useful results.<sup>3b</sup> These numerical results have been obtained either by finite-difference (FD) techniques<sup>2</sup> or by variational methods (e.g., the finite element method<sup>4</sup>). Because of the generality of the stochastic-Liouville approach and the broad applicability of numerical solutions, complex models and chemical systems yielding CIDN(E)P effects can be studied where analytic mathematical treatments become difficult. These include CIDEP (as already noted), as well as studies of CIDNP for  $J(r) \neq 0$ . CIDN(E)P in low magnetic fields,<sup>5</sup> and when orientation dependent effects of spin exchange and reaction dynamics are included in the analysis."

The present study attempts to extend the understanding of CIDN(E)P to reactions and interactions between radical species constrained to planar surfaces, micellar surfaces, membranes and, in general, any physical circumstance where two-dimensional diffusion of the radicals would take place. The use of the term two dimensional thus only signifies the diffusive characteristics and not necessarily the physical surroundings in our treatment. We do restrict this present study to radical motion that can be described by Brownian diffusion (i.e., as in a fluid layer). It is important to note that the numerical methods do allow the study of, for example, diffusion of adsorbed atoms on solid surfaces<sup>7</sup> by jumps that traverse potential barriers.

This study of CIDN(E)P in two-dimensional systems also employs numerical solutions of the SLE, although approximate forms for some aspects of CIDNP linked with recombination kinetics can be developed.<sup>8</sup> However, because of the unusual feature that the probability is unity for two diffusing (i.e., randomly moving) particles to undergo a future collision in dimensions lower than three,<sup>9</sup> an entirely different analysis of the time dependence is required compared to that for the threedimensional studies. We shall first consider a simple "idealized" two-dimensional model that readily yields CIDN(E)P results clearly illustrating the implications of this unusual feature. This idealized model is that of two-dimensional relative diffusion of a radical pair on an infinite surface (i.e., an unbounded sheet or slab) with magnetic and exchange interactions and geminate recombination reactions, but without any spin relaxation, radical scavenging reactions, or escape from the surface. Deutch<sup>10</sup> previously attempted to explain nuclear polarization for such an idealized state.

Recombination kinetics in "realistic" two-dimensional systems will be considered using the appropriate modification of the three-dimensional formalism,<sup>2</sup> in which the complexities involved in the reduction of dimensionality become apparent. This analysis clearly points out that the time-dependent forms of all CIDN(E)P quantities (or their Laplace-transformed analogues) are essential for understanding two-dimensional magnetic and kinetic effects. This is unlike the three-dimensional results for which the long-time asymptotic results were sufficient. Approximate empirical formulas for these

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quantities may be determined from the numerical results. It is then convenient to use these results to analyze possible experiments in real systems of finite physical extent or where scavenging reactions are present, etc. Preliminary results of the numerical study have already been reported.<sup>1b,11</sup>

CIDN(E)P polarizations for two-dimensional systems could be observed in situations where two-dimensional reaction dynamics is believed to occur. The advantages for chemical kinetics of a reduction in the dimensionality have been discussed previously by Adam and Delbrück<sup>9b</sup> and others.<sup>12,13</sup> NMR and ESR studies<sup>14,15</sup> of spin relaxation and dipolar interactions in two dimensions have also been performed theoretically and experimentally. These studies illustrate the complexities found in treating time-dependent processes in a twodimensional fluid.

We discuss in Sec. II the limiting results appropriate for the "idealized model." The SLE and its solution in two dimensions is outlined in Sec. III. The realistic time-dependent results (actually their Laplace transforms) appear in Secs. IV (CIDNP), V (CIDEP), and VI (Heisenberg spin exchange, HE). We then illustrate how these time-dependent results would lead to meaningful physical observables in real experiments in Secs. VII and VIII. In particular, Sec. VII deals mainly with initial polarization processes, while Sec. VIII deals with polarization processes initiated by random bimolecular collisions. Further discussion and summary appear in Sec. IX.

#### **II. AN IDEALIZED MODEL**

Consider an idealized model which contains two radicals diffusing within a slab of fluid of finite thickness (chosen to be the particle diameter, d) but where the movement of the particle centers is constrained to a plane. These radicals are only allowed to move within the slab with no chance of escape. The relative diffusion of the radicals is assumed to be described by a single relative diffusion coefficient equal to the sum of the individual radical diffusion coefficients. Thus, in this work we are ignoring interesting effects from timedependent diffusion coefficients which are another manifestation of the two dimensionality.<sup>16</sup> Each radical contains one unpaired electron  $(S = \frac{1}{2})$  and nuclei with known spin and hyperfine coupling constants. Upon placing such a "sample" in a static, large magnetic field of known magnitude the radicals experience Zeeman interactions as well as the hyperfine and spin exchange interactions. The large magnetic field splits the  $m_s = \pm 1$ triplet energy levels of the radical pair from the  $m_s = 0$ levels sufficiently to allow their omission from the following analysis. [The  $T_{\star}$  states do enter into discussions of CIDN(E)P from reactions carried out in low magnetic fields or in very viscous systems.<sup>5</sup>] The exchange interaction, J(r) is realistically assumed to be of finite extent with an exponential dependence upon distance similar to that used earlier.<sup>2, 4-8</sup> When the two radicals come into contact (or more precisely are within a given distance  $\Delta r_k$  of each other) a pseudo-first-order spin-selective reaction occurs with

a specific rate constant k. Radical reactions will usually be restricted to contact collisions involving radicals existing in the singlet (bonding) electronic state. No external boundaries, scavenging reactions, or sink factors will be included in our idealized model.

If we were to follow the precedent of the three-dimensional CIDN(E)P treatment,  $^2$  we would be interested in calculating only the long-time asymptotic values of all CIDN(E)P quantities as functions of the different kinetic and magnetic parameters entering our model. This may be attributed to the fact that any two particles diffusing in a three-dimensional liquid have a very small probability (< 1) of coming in contact in the future after achieving a large enough separation. This means that two particles encountering each other in a liquid may separate and then undergo several re-encounters before finally diffusing apart, never to re-encounter again. Noyes<sup>17</sup> first calculated that particles diffusing in normal liquids have about a 50% chance of re-encountering at least once again after having initially participated in an encounter and separated to a distance twice their contact diameter. Thus, after a sufficient period of time, the two radicals (if they have not combined) will separate permanently and the chemical and spin properties dependent on their encounters will approach their asymptotic (i.e., long-time) values.

In the discussion above, we have used the terminology of Pedersen and Freed,<sup>2</sup> which differs somewhat from that of Noyes.<sup>17</sup> The term "encounter" applies when two particles come into close enough proximity in a liquid such that exchange or other interactions between the radical pair are not negligible. During such an encounter the radicals could actually come in contact. In three dimensions Pedersen and Freed referred to the initial encounter and subsequent re-encounters before the radicals finally separate as the "collision." (This differs from Noyes usage of the term collision as the event when two particles actually come in contact, so there can be many such collisions during each encounter. We will refer to this type of event simply as a radicalpair contact.)

A pair of radicals, or particles, diffusing in a twodimensional system always has unit probability<sup>9</sup> of reencountering (as well as of coming into contact) regardless of the extent of their initial separation (as long as there is no interference to their relative diffusion; this is the case for our idealized state). Using the definitions above, we see that in our idealized model two particles can always be strictly considered as a collision pair, since the particles will continue to experience reencounters for all time. The period during which the particles have been experiencing encounters, then, is just equal to the real elapsed time after their formation. Also, this will continue as time progresses until some reaction (or absorbing) process intercedes. Again we note, in our idealized model, all intervening chemical and physical processes have been excluded. We thus have a model where a radical pair will come into contact repeatedly and thus ultimately react to form a geminate recombination product provided only that the reaction probability is greater than zero.

Because we wish to emphasize CIDN(E)P, we will concern ourselves with the case of a single radical pair formed in a well-defined quantum state on some surface. The prediction of CIDN(E)P observables for  $t \rightarrow \infty$ in this case is straightforward. As long as a recombination reaction is allowed (i.e., there exists a nonzero pseudo-first-order rate constant for reactions upon contact) there will always be a sufficient number of contacts to drive the reaction to completion.<sup>10</sup> Thus we may write

$$\Lambda^{(2)} \equiv \lim_{t \to \infty} \Lambda^{(2)}(t) = 1 , \qquad (1)$$

where the superscript notes the dimensionality. Here  $\Lambda^{(2)}(t)$  is the time-dependent probability that a radical pair has reacted. Equation (1) implies then that  $\tau_1$ , the effective lifetime of the radical-pair collision,<sup>2</sup> is

$$\tau_1 \equiv \lim_{t \to \infty} \tau_1(t) = \infty \quad . \tag{2}$$

Other important CIDNP quantities for this model attain limiting values by analogous (i.e., infinite re-encounter) arguments. The probability  $\mathfrak{T}^*(t)$  that the radical pair, if initially in a triplet state, will later react in the singlet state reaches its maximum (asymptotic) value due to repeated collisions. For nonzero magnetic interactions,

$$\mathfrak{F}^{*(2)} = \lim_{t \to \infty} \mathfrak{F}^{*(2)}(t) = 1$$
 (3)

Nuclear-spin polarizations then follow from

$$\mathfrak{F}^* \equiv \lim_{\Lambda \to 1} \mathfrak{F}(T_0) ; \qquad (4a)$$

thus from Eqs. (3) and (4a)

$$\mathcal{F}^{(2)} = \mathcal{F}^{*(2)} = 1$$
, (4b)

where the  $T_0$  in parentheses refers to a triplet initial condition. Equation (4b) is a significant result since it specifies that all nuclear spin configurations will be populated equally provided there is a nonzero spin-dependent reaction rate and finite Q mixing of spin states. But it is well known that CIDNP enhancements are observed from geminate recombination products only when there is a net preferential effect on the rate of recombination for selected (and not all) nuclear spin states [cf. Ref. 2 and Chap. III of Ref. 2(a)]. Thus we conclude that for our idealized model there can be no CIDNP signal enhancements in two dimensions.

By similar argument we can determine the CIDEP for the two interacting radicals. During each encounter between these two radicals, i.e., when they are close enough that a spin exchange interaction exists, there will be finite probabilities for (1) the generation of electron spin polarization by a two step procedure<sup>2</sup> which involves consecutive Q mixing (of  $\rho_{T0T0}$  and  $Im\rho_{ST0}$ ) and exchange modulation effects (involving  $Im \rho_{ST_0}$  and  $\operatorname{Re}\rho_{ST_0}$ ), as well as (2) spin depolarization by the reverse process which randomizes any initial polarization due to the random life time of each encounter pair. One finds in three dimensions, that (1) goes linearly with  $J_0 \tau_J$  and (2) goes as  $(J_0 \tau_J)^2$  for  $|J_0 \tau_J| \ll 1$  where  $\tau_J$ represents an effective encounter lifetime for the whole collision summed over all the encounters, and  $J_0$  is a measure of the strength of the exchange interaction. By analogy to Eq. (1a), we can write for our idealized two-dimensional model that [we later recognize  $\tau_J$  as  $\tau_1(\lambda)$  of Ref. 2]

$$\tau_{J} = \lim_{t \to \infty} \tau_{J}(t) = \infty .$$
 (5)

We note that the actual mechanism of mixing of the spin states of the encounter radical pair due to J(r) should be independent of dimension (except for the meaning of  $\tau_J$ ), so that the same power law on  $J_0$  (or  $|J_0\tau_J|$ ) is to be expected in two dimensions vs three dimensions. We would then conclude that the electron-spin polarization on each radical will be completely randomized (except for the residual Boltzmann polarization due to the large magnetic field).

If we label our two interacting radicals a and b, then the selective polarization of the radicals is

$$P_a^{(2)}(\infty) \equiv \lim_{t \to \infty} P_a^{(2)}(t) = 0$$
(6)

and

$$P_b^{(2)}(\infty) \equiv \lim_{t \to \infty} P_b^{(2)}(t) = 0 .$$
 (7)

These results, Eqs. (6) and (7), show that in the absence of radical scavenging or escape in the fluid system, etc., one would obtain no selective electronic polarization via CIDEP. This is not the result for three-dimensional cases where  $P_a^{(3)}(\infty)$  has some finite value, yielding observable ESR signals, though  $P_a^{(3)}(\infty) = -P_b^{(3)}(\infty)$  in high fields.<sup>2</sup>

Obviously, the discussion of two-dimensional CIDN(E)P in terms of the variables used in the analysis of threedimensional fluids does not lead to any observable spin polarization effects. One would note, though, that any chemical scavenging reaction (i.e., where the interacting radicals are forced to react with other chemical species), escape rate (e.g., from the surface of a micelle into the surrounding solution), or boundary effects can terminate the interaction of the two radicals. This would reduce the number of particle encounters to some finite value and alter the above results. The frequency of scavenging reactions will be a function of the surface concentration of scavenging "sinks"<sup>18</sup> or the distance to a boundary which interrupts particle diffusion in some manner. The CIDNP quantities  $\Lambda^{(2)}$  and  $\mathfrak{F}^{*(2)}$  found in the idealized state will then obviously form the upper limit to their actual value in a real chemical system. Similarly, observed electronic polarizations will always be (equal to or) greater than those of the idealized state since complete spin randomization need not take place.

One must then solve for the time dependence of CIDN(E)P quantities for a realistic and useful analysis. Because of the computational ease associated with the Laplace transformed CIDN(E)P problem we will obtain our results in Secs. IV, V, and VI as a function of the Laplace transform variable, s. From these results we will be able to obtain values of the CIDN(E)P quantities needed for the realistic cases in Secs. VII and VIII.

# III. THE STOCHASTIC LIOUVILLE APPROACH FOR TWO DIMENSIONS

Since the basics of the numerical solution of the SLE are given elsewhere,<sup>2</sup> we need only point out those aspects of importance to our two-dimensional analysis. A typical solution requires the calculation of the elements of the spin density matrix  $\rho(\mathbf{r}, t)$ , which include all

of the quantum mechanical and classical diffusive information. The time evolution of these processes is governed by the SLE,

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = -i\mathcal{H}^{\mathbf{r}}(\mathbf{r})\rho(\mathbf{r},t) + D\Gamma_{\mathbf{r}}\rho(\mathbf{r},t) + \mathcal{K}_{\mathbf{r}}\rho(\mathbf{r},t) , \qquad (8)$$

where we use the superoperator notation  $A^*B \equiv [A, B]$ .  $\mathfrak{K}(\mathbf{r})$  is the spatially dependent Hamiltonian operator,  $\Gamma_{\mathbf{r}}$  is the diffusion operator for the relative motion of the radical pair which becomes  $\Gamma_{\mathbf{r}}$ , i.e., radial diffusion, if only isotropic diffusion is assumed, as is the case in this work. The distance of closest approach (the contact distance) is signified by d. Radical reactions during contacts are contained in the spin-selective reaction operator,  $\mathfrak{K}_{\mathbf{r}}$ . We will consider the diffusion of the particle centers to lie on a plane (at z = 0). Then, we can simplify Eq. (7) by using cylindrical coordinates, so

$$\rho(\mathbf{r},t) = (1/2\pi) \int_{-\infty}^{\infty} \delta(z) dz \int_{0}^{2\pi} d\theta \,\rho(\mathbf{r},t) , \qquad (9)$$

then  $\Gamma_r$  simplifies to the radial diffusion operator,

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$$\Gamma_{r} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial^{-}}{\partial r} \right) + \frac{1}{k_{B}T} \frac{\partial}{\partial r} \left[ F(r)^{-} \right], \qquad (10)$$

where we have included an r-dependent force of interaction between the radical pair, F(r), which is taken as spin independent for simplicity.<sup>2</sup> Also

$$|S\rangle |T_0\rangle$$
  

$$\mathcal{K}(r) = \begin{pmatrix} -2J(r) & Q \\ Q & O \end{pmatrix},$$
(11)

where S and  $T_0$  are indices denoting the singlet or triplet  $(m_s=0)$  states, respectively. In Eq. (11), Q is one-half the difference in the ESR frequencies of the radicals (employed here for reaction in high magnetic fields) and J(r) is chosen to follow:

$$J(\gamma) = J_0 e^{-\lambda (r-d)} , \qquad (12)$$

with  $\lambda = (5 \ln 10)/r_{ex}$ , using  $r_{ex}$  as a measure of the exchange region  $(r_{ex} \approx d)$ . The form of  $\mathcal{K}_r$  (now only radially dependent) is taken as<sup>2</sup>

$$\boldsymbol{x}_{r} \rho(r, t) = -k(r) \left| \boldsymbol{S} \right\rangle \rho_{\boldsymbol{S} \boldsymbol{S}}(r, t) \left\langle \boldsymbol{S} \right| , \qquad (13)$$

where one usually employs  $k(r) = k\delta(r-d)$ . The term  $\rho_{ij}(r,t)$  represents the *ij*th element of the density matrix,  $\langle i | \rho(r,t) | j \rangle$ . The advantage of a numerical approach is that J(r) and k(r) may be represented by functions of finite extent without affecting the ease of solution.

By Laplace transforming Eq. (8) we can eventually use inversion methods of solution rather than having to treat the time derivative explicitly. Thus we will employ

$$\rho_{ij}(r,s) = \int_0^\infty e^{-st} \rho_{ij}(r,t) dt .$$
 (14)

We will utilize the dimensionless quantities:  $y \equiv r/d$ ,  $\sigma \equiv sd^2/D$ ,  $\kappa = kd^2/D$ ,  $q = Qd^2/D$ ,  $j_0 = J_0d^2/D$ , and f(y)  $\equiv dF(r)/k_BT$ , so we can now write Eq. (8) transformed according to Eq. (14), as

$$\sigma \rho_{kl}(y,\sigma) - \rho_{kl}(y,0) = \sum_{all \ i \ and \ j} \left\{ -i(\mathcal{H}_{kl} \ \delta_{jl} - \delta_{kl} \ \mathcal{H}_{jl}) + \delta_{kl} \ \delta_{jl} \left( \frac{\partial^2}{\partial y^2} + \frac{1}{y} \ \frac{\partial}{\partial y} + \frac{\partial f(y)}{\partial y} + f(y) \ \frac{\partial}{\partial y} \right) - \kappa \ \delta_{kl} \ \delta_{jl} \ \delta_{kS} \ \delta_{kS} \left\} \rho_{ij}(y,\sigma) , \qquad (15)$$

where the matrix element  $\mathcal{K}_{ij} \equiv \langle i | \mathcal{K}(r) | j \rangle d^2 / D$  and  $\delta_{ij}$  is the Kronecker delta  $\langle \delta_{ij} = 1$  for i = j, 0 for  $i \neq j$ ). Equation (15) is then solved by the use of a finite difference approximation of the  $\Gamma_{\tau}$  operator. This involves the specification of  $\rho$  only at selected radial points (i.e., nodes) so, for example, at the *m*th node we will calculate  $\rho_{ij}(y_m, \sigma)$ . Construction of the matrix equation follows usual procedures<sup>2,5</sup> yielding

$$[\sigma \mathbf{1} - \mathbf{K}' - \mathbf{W}' + i\Omega]\rho(\sigma) = \rho(0) . \tag{16}$$

The matrices  $\mathbf{K}'$  and  $\Omega$  contain elements formed from the first and last terms of the RHS of Eq. (15). The components of the vector  $\rho(\sigma)$  are the spin density matrix elements at each node. For two-dimensional diffusion the "transition" matrix  $\mathbf{W}'$  may be created by the multiplication of each element of the basic matrix  $\mathbf{W}$  by a  $4 \times 4$  unit matrix. The elements of  $\mathbf{W}$  for planar radial diffusion are

$$W_{0,0} = -\frac{1}{\Delta y} \left( 1 + \frac{2}{\Delta y} \right) + \frac{(1 + \Delta y) f(1)}{\Delta y} , \qquad (17a)$$

$$W_{0,1} = \frac{1}{\Delta y} \left( 1 + \frac{2}{\Delta y} \right) + \frac{f(0)}{\Delta y} , \qquad (17b)$$

$$W_{j,j\pm 1} = \frac{1}{\Delta y} \left( \frac{1}{\Delta y} \pm \frac{1}{2y_j} \right) \pm \frac{f(j)}{2\Delta y} , \qquad (17c)$$

$$W_{j,j} = -\frac{2}{(\Delta y)^2} + \frac{1}{2\Delta y} \left[ \frac{y_{j+1}}{y_j} f(j+1) - \frac{y_{j-1}}{y_j} f(j-1) \right],$$
(17d)

where 0 < j < N and  $\Delta y = y_{i+1} - y_i$  (equal) for all *i*, but

$$W_{N,N-1} = \frac{2}{\Delta y} \left( \frac{1}{\Delta y} - \frac{1}{2y_N} \right) - \frac{f(N)}{\Delta y} , \qquad (17e)$$

and

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$$W_{N-1,N} = W_{N,N} = 0 . (17f)$$

These "transition probabilities" obey the condition of conservation of total probability:

$$\sum_{i=0}^{N} V(i) W_{i,j} = 0 \text{ for } j = 0, 1, \dots, N$$
(18)

as required. Here V(i) is a dimensionless "volume factor" given by

$$V(i) = y_i \Delta y \quad \text{for } 0 < i < N , \qquad (19a)$$

$$V(0) = \Delta y / 2 , \qquad (19b)$$

$$V(N) = y_N \Delta y/2 . \tag{19c}$$

The transition matrix elements of Eqs. (17a) and (17b) are for an inner reflecting wall while those for Eqs. (17e) and (17f) are for an outer absorbing boundary at  $y_N$ . As we have already pointed out, the value of  $y_N$  always plays an important role (for  $s \approx 0$ ) in two dimensions. However, if we look at short-time effects or al-

ternatively s > 0, then  $y_N$  may be chosen large enough so as not to interfere with the diffusive effects. One significant computational observation<sup>2b</sup> was that all finite differences  $\Delta y$  must be chosen equal in order not to create artificial reflections toward the origin. Thus the nodal distances (with  $y_0 = 1$ ) are simply

$$y_{j} = 1 + j\Delta y \quad \text{for } 0 < j < N . \tag{20}$$

The solution of Eq. (16), developed from Eqs. (17)-(20), is obtained by employing Gaussian elimination with partial pivoting since Eq. (16) is ill conditioned. The calculations were carried out on an IBM 370/168 computer and PDP 11/34 minicomputer.

After the calculation of the LHS vector,  $\rho(\sigma)$ , of Eq. (16) the quantities  $\hat{\sigma}(\sigma)$  (a Laplace transform of the total probability that the radicals have not reacted for given value of  $\sigma$ ) and  $\hat{P}_a(\sigma)$ , (a Laplace transform of the electron spin polarization of radical "a") can be found from the FD equations<sup>2</sup>

$$\hat{\varphi}(\sigma) \equiv \sigma \varphi(\sigma) = \sigma \sum_{i=0}^{N} V(i) \left[ \rho_{SS}(y_i, \sigma) + \rho_{T_0T_0}(y_i, \sigma) \right], \qquad (21)$$

$$\hat{P}_{a}(\sigma) \equiv \sigma P_{a}(\sigma) = -2\sigma \sum_{i=0}^{n} V(i) \operatorname{Re}\left[\rho_{ST_{0}}(y_{i}, \sigma)\right].$$
(22)

CIDNP results are also based on Eq. (21) but in the form

$$\hat{\mathfrak{F}}(\sigma) = 1 - \hat{\mathfrak{P}}(\sigma)$$
, (23)

from which we can find for singlet initial condition (S):

$$\widehat{\Lambda}(\sigma) \equiv \lim \widehat{\mathfrak{F}}(\sigma, S) \equiv \mathfrak{F}_0(\sigma, S) , \qquad (24)$$

and for a triplet initiation condition  $(T_0)$ :

$$\hat{\mathfrak{F}}^*(\sigma) \equiv \lim \hat{\mathfrak{F}}(\sigma, T_0) . \tag{25}$$

All of the above quantities relate to general CIDN(E)P results so we shall use a superscript, as seen in Eqs. (1)-(7), to denote the dimensionality. Below we will examine the results for  $\hat{\Lambda}^{(2)}(\sigma)$ ,  $\hat{\mathcal{F}}^{*(2)}(\sigma)$ , and  $\hat{P}_{4}^{(2)}(\sigma)$ , and illustrate how they may be related to observables.

The important effects of forces between the radical pair for three-dimensional pair distribution functions has already been demonstrated.<sup>2a</sup> In particular for two dimensions one may represent the radially symmetric potential of mean force U(r) between the radical pair by the expression

$$f(y)\hat{e}_{\mathbf{r}} \equiv (d/kT) \nabla U(r) = (d/kT) \left[ \partial U(r) / \partial r \right] \hat{e}_{\mathbf{r}} , \qquad (26)$$

where  $\hat{e}_r$  is a unit vector in the x-y plane. If the radicals are charged, the U(r) would represent the (shielded)-Coulombic interactions; if the diffusion is in a dense medium (e.g., a membrane interior or a monolayer of gas adsorbed on a solid surface) then one should employ the equilibrium pair correlation function g(r), from which we can obtain the U(r) by the expression  $U(r)/kT \equiv -\ln g(r)$ .

One could also represent the effects of periodic binding sites characterizing a crystalline surface on the relative diffusion by means of a periodic g(r) characteristic of the surface. (For strong potential wells the use of jump diffusion models would be convenient. Methods for including jump models in the SLE are discussed by Freed and Pedersen<sup>2a</sup> for three dimensions and an analogous approach would apply for two dimensions.) In the final analysis, however, the periodic properties are probably important in CIDN(E)P problems only for values of  $r \sim d$ , so a modified g(r) in which the periodic potentials for  $r \sim d$  (or  $y \sim 1$ ) are reasonably well included should be sufficient.

In the following sections we discuss results for which U(r) = 0 except for the hard-sphere repulsive barrier at r = d (y = 1) which is well represented by the reflecting wall.

# IV. CIDNP ARISING FROM REACTIONS ON A SURFACE

We have noted in the above discussion that at least two types of termination processes may exist in a twodimensional system. Either a radical sink or some type of absorbing boundary may interfere with normal diffusion and produce CIDNP results different from the idealized case. The effects of both termination processes may easily be decoupled. That is, in our numerical calculations we can choose  $\sigma \approx 0$  and obtain results dependent on  $y_N$ , the absorbing (or more exactly, collecting) outer boundary, cf. Eqs. (17e) and (17f). Similarly, we can choose  $y_N > 10^3$ , so that the CIDNP process is not affected by the outer boundary during rather long time periods  $\tau \sim \sigma^{-1}$ . More precisely the  $\sigma$  dependence of the solutions (i.e., the Laplace transforms) may be interpreted as the CIDN(E)P values obtained for those "radical pairs" that are scavenged by a (pseudo)-first-order rate process with rate constant (in dimensionless units)  $\kappa = \sigma$  (see below). Since this is an inverse half-life, we may, alternatively, crudely relate a time as  $\tau \sim \sigma^{-1}$ . The more rigorous use of the Laplace transformed variables [cf. Eqs. (21)-(25)] is discussed in Secs. VII and VIII.

A study of both types of calculations leads to a relation between values of  $y_N$  in the first type of calculation and values of  $\sigma$  in the second type such that both methods yield CIDN(E)P results that are equal (or comparable). This relation was given previously, <sup>2b, 11</sup> and is

$$t \approx s^{-1} = \left[ \ln\left(\frac{r_N}{d}\right) - \frac{1}{2} \right] (r_N)^2 / 4D$$
 (27a)

or in dimensionless units

$$\tau \approx \sigma^{-1} = \frac{(y_N)^2}{4} (\ln y_N - \frac{1}{2})$$
 (27b)

Here  $\tau$  represents the time needed for a particle that is initially located very near the center of a large circular slab  $(y_N \gg 1)$  to reach the outer boundary. This is the situation that is simulated in our calculations. Once we have this relation we need only obtain CIDN(E)P results as a function of  $\sigma$  (with  $y_N \gg 1$ ), and then, whenever needed, Eq. (27) may be used to obtain the result as a function of  $y_N$  (or  $r_N$ ). However, we shall see that the  $\sigma$ -dependent results will usually be the more useful.

In the study of three-dimensional CIDE(N)P by Pedersen and Freed, general relations exactly obeyed by the quantities  $\Lambda$ ,  $\mathfrak{F}$ , and  $P_a^{\infty} [= P_a(\infty)$  in this work] were established<sup>2a</sup> (for  $\gamma_I = d$ ). We have studied the extension of these relations to the two-dimensional problem, and we have confirmed their applicability in  $\sigma$  space. Thus we may write

$$- [\hat{\mathfrak{F}}^{(2)}(S,\sigma) - \hat{\mathfrak{F}}_{0}^{(2)}(S,\sigma)] = - [\hat{\mathfrak{F}}^{(2)}(S,\sigma) - \hat{\Lambda}^{(2)}(\sigma)] = [1 - \hat{\Lambda}^{(2)}(\sigma)] \hat{\mathfrak{F}}^{(2)}(T_{0},\sigma)$$
(28)

and

 $[\hat{\mathfrak{F}}^{(2)}(\mathbf{RI}, \sigma) - \hat{\mathfrak{F}}^{(2)}_{0}(\mathbf{RI}, \sigma)] / \hat{\mathfrak{F}}^{(2)}_{0}(\mathbf{RI}, \sigma) = \hat{\mathfrak{F}}^{(2)}(T_{0}, \sigma) , \qquad (29)$ 

where

$$\hat{\mathfrak{F}}_{0}^{(2)}(\mathbf{RI},\sigma) = \frac{1}{2} \hat{\Lambda}^{(2)}(\sigma)$$
 (30)

and RI stands for random initial condition.

The quantity  $\hat{\mathfrak{F}}^{(2)}(\sigma)$  appears in the exact relation  $\hat{\mathfrak{F}}^{(2)}(T_0,\sigma) = \hat{\Lambda}^{(2)}(\sigma) \hat{\mathfrak{F}}^{(2)*}(\sigma) [1 + \hat{\mathfrak{F}}^{(2)*}(\sigma) (1 - \hat{\Lambda}^{(2)}(\sigma))]^{-1}$ .

(31) It is thus seen from Eqs. (21), (28), and (30) that all the relevant two-dimensional CIDNP results (cf. Sec. VII) follow immediately from a knowledge of  $\hat{\Lambda}^{(2)}(\sigma)$  and  $\hat{\mathfrak{F}}^{(2)*}(\sigma)$ . (Note that the equivalent  $\sigma$  dependent expressions apply in 3D even though they have previously only been give for  $\sigma = 0$ .)

We have found that our numerical results for  $\hat{\Lambda}^{(2)}(\sigma)$  may be approximated by

$$\hat{\Lambda}^{(2)}(\sigma) \cong \frac{\kappa \tau_I \, \mathcal{L}(\sigma)}{1 + \kappa \tau_1 \, \mathcal{L}(\sigma)} , \qquad (32)$$

where  $\mathfrak{L}(\sigma)$  is defined by

$$\mathcal{L}(\sigma) \equiv \ln\left[1 + \frac{4}{3}\sigma^{-1/2}\right], \qquad (33)$$

so  $\lim_{\sigma \to 0} \mathfrak{L}(\sigma) \to \infty$ , and where  $\tau_I \equiv \Delta y/2$  is the dimensionless lifetime of a colliding pair of particles [in the notation of Ref. 2(a),  $\tau_I \equiv \tau_1 D/d^2$ ].

The mathematical derivation of  $\Lambda^{(2)}(t)$  has recently been considered by Kofman and Burshtein, <sup>8a</sup> although no exact analytic forms could be obtained<sup>19</sup> (cf. Sec. IV of their work). Our exact numerical results for  $\Lambda^{(2)}(\sigma)$ and the values calculated from Eq. (32) are shown in Table I. These results confirm that the form of Eq. (32) is correct to within 5% for  $\sigma \leq 0.016$ , but is less accurate for short times (i.e.,  $\sigma \geq 1$ ). Equation (32) also has the required property that as  $\sigma \rightarrow 0$  (i.e., very

TABLE I.  $\hat{\Lambda}^2(\sigma)$  for several values of  $\kappa$ .<sup>**a**,**b**</sup>

σ/1.6	$\kappa = 0.016$	1.6	160.
0.005	0.0013(0.0014)	0,11(0,12)	0,93(0,93)
0.01	0.0011(0.0012)	0.10(0.11)	0.92(0.92)
0.05	0.00077(0.00087)	0.072(0.080)	0.89(0.90)
0.1	0.00064(0.00073)	0,060(0,068)	0.86(0.88)
0.5	0.00038(0.00046)	0.037(0.044)	0.79(0.82)
1.0	0.00029(0.00036)	0.028(0.035)	0.75(0.78)

<sup>a</sup>Finite difference results found using  $d^2/D = 1.6 \times 10^{-10}$ sec,  $\Delta y = 0.0625$ ,  $q = j_0 = 0$  and a singlet initial condition. A value of  $y_N = 26$  was used in these computations so that the outer boundary would not affect the number of possible re-encounters allowed for the value of  $\sigma$  employed. <sup>b</sup>The numerical result is listed first with the approximate result calculated from Eq. (32) following it in parentheses. long times) one obtains the asymptotic result characteristic of the idealized state, i.e.,  $\hat{\Lambda}(\sigma-0)=1$ . We wish to note that our analysis of the numerical calculations to yield expressions like that of Eq. (32) was significantly aided by the asymptotic results of Eqs. (1)-(7).

It is also possible to express  $\Lambda^{(2)}$  [cf. Eq. (1)] for finite  $y_N$  in the limit  $\sigma \rightarrow 0$ , <sup>11</sup> in terms of a fairly simple and accurate expression that is very similar to the form for  $\Lambda^{(3)}$ . That is, we may write

$$\Lambda^{(n)}(y_N) = \frac{\kappa \tau_I^{(n)}}{1 + \kappa \tau_I^{(n)}} , \qquad (34)$$

where  $\tau_I^{(3)} = \tau_I$  but  $\tau_I^{(2)} \cong \tau_I \ln y_N$  and  $\tau_I$  is given above. This result suggests that  $\tau_I^{(2)}$ , the effective lifetime of the reacting pair, increases asymptotically as  $\ln y_N$ , becoming infinite as  $y_N \to \infty$  consistent with Eq. (2) for the idealized model. This result may perhaps be better understood by examining the probability  $(t_f)$  that radicals initially separated by distance  $y_I$  will re-encounter for finite  $y_N$ :

$$t_f(y_I, y_N) = 1 - \ln(y_I) / \ln(y_N)$$
 (35)

So as  $y_N \rightarrow \infty$ ,  $t_f \rightarrow 1$  also consistent with the idealized model. Thus, as  $y_N \rightarrow \infty$  re-encounters will continue forever regardless of the initial separation, thus yielding an infinite  $\tau_I^{(2)}$ . In the case of Eq. (32) we can think of an effective  $\tau_I^{(2)}(\sigma) \cong \tau_I \mathcal{L}(\sigma)$  which becomes infinite as  $\sigma \rightarrow 0$ . Also consistent with our above result, Eq. (35), we have found<sup>20</sup>

$$\hat{t}_f(y_I,\sigma) \approx 1 - \frac{\ln y_I}{\mathcal{L}(\sigma)}$$
(36)

valid for  $\mathcal{L}(\sigma) > \ln y_I$ . The fact that relations for  $\Lambda^{(2)}(y_N)$ appear simple and accurate compared to those for  $\hat{\Lambda}^{(2)}(\sigma)$  is probably connected with the (transcendental) nature of Eq. (27) which links the two types of expression. [Note that one can relate any result such as  $\hat{\mathfrak{F}}^{*(2)}(\sigma)$  evaluated at  $y_I = 1$  with  $\hat{\mathfrak{F}}^{*(2)}(\sigma, r_I = d) = \hat{t}_f(y_I, \sigma)$  $\times \hat{\mathfrak{F}}^{*(2)}(\sigma, r_I)$  for arbitrary  $y_I$ . That is,  $\hat{t}_f(y_I, \sigma)$  plays the role of a "transfer factor."<sup>2</sup>]

In the case of  $\mathfrak{F}^{*(2)}(y_N)$  and  $\hat{\mathfrak{F}}^{*(2)}(\sigma)$  the former can again be described more easily by an approximate formula.<sup>11</sup> However, we are presently more interested in the latter, which we may approximate as

$$\hat{\mathfrak{F}}^{*(2)}(\sigma) \approx \frac{\frac{1}{2} \sigma^{-1,7} q^2}{1 + \frac{1}{2} \sigma^{-1,7} q^2 / \mathfrak{F}^7}, \qquad (37)$$

where

$$\widehat{\mathfrak{F}}' = \frac{\mathfrak{L}(\sigma) q^{0,2}}{1 + \mathfrak{L}(\sigma) q^{0,2}} .$$
(38)

Thus for  $q/\sigma \gg 1$  (i.e., long times and/or large hyperfine interactions) one has

$$\hat{\mathfrak{F}}^{*(2)}\left(\frac{\sigma}{q}\ll 1\right)\approx \hat{\mathfrak{F}}' \quad (39)$$

In the limit  $\sigma \sim 0$  one therefore obtains  $\widehat{\mathfrak{F}}^{*(2)}(\sigma) + 1$  in accordance with Eq. (3). The predictions of Eq. (37) are compared with some exact numerical results in Table II. The functional dependence on q is seen to be different than the  $q^{1/2}$  dependence for  $\widehat{\mathfrak{F}}^{*(3)}(\sigma \approx 0)$  [which is reasonably well approximated by the expression  $\frac{1}{2}q^{1/2}/(1+\frac{1}{2}q^{1/2})$ ].<sup>2b</sup> The functional dependence of  $\mathfrak{F}^{*(2)}(y_N)$  on

TABLE	п.	<b>ĵ</b> *'	<sup>(2)</sup> (σ)	versus	q.ª,
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q/1.6=					
σ/1.6	10-4	10-3	10*2	10-1	1
0.005	$5.1 \times 10^{-5} (4.7 \times 10^{-5})$	$4.9 \times 10^{-3}$ (4.6×10^{-3})	0.15(0.25)	0.45(0.65)	0.74(0.75)
0.01	$1.9 \times 10^{-5}$ $(1.3 \times 10^{-5})$	1.9×10 <sup>-3</sup> (1.4×10 <sup>-3</sup> )	9.2×10 <sup>-2</sup> (0.11)	0.40(0.60)	0.72(0.73)
0,05	$1.2 \times 10^{-6}$ (9.4×10 <sup>-7</sup> )	$1.2 \times 10^{-4}$ (9.4×10 <sup>-5</sup> )	$1.1 \times 10^{-2}$ (9.2×10 <sup>-3</sup> )	0.23(0.35)	0.61(0.65)
0.1	$3.3 \times 10^{-7}$ (2.9×10 <sup>-7</sup> )	$3.3 \times 10^{-5}$ (2.9×10 <sup>-5</sup> )	$3.3 \times 10^{-3}$ (2.9×10 <sup>-3</sup> )	0.14(0.18)	0.54(0.60)
0.5	$1.8 \times 10^{-8}$ (1.9×10 <sup>-8</sup> )	$1.8 \times 10^{-6}$ (1.9×10^{-6})	$1.8 \times 10^{-4}$ (1.9×10 <sup>-4</sup> )	$1.7 \times 10^{-2}$ $(1.8 \times 10^{-2})$	0.32(0.39)
1.0	$4.9 \times 10^{-9}$ (5.8×10 <sup>-9</sup> )	$4.9 \times 10^{-7}$ (5.8×10 <sup>-7</sup> )	$\begin{array}{c} 4.9 \times 10^{-5} \\ (5.8 \times 10^{-5}) \end{array}$	4.8×10 <sup>-3</sup> (5.7×10 <sup>-3</sup> )	0,20(0.25)

<sup>a</sup>Finite difference results found using  $\Delta y = 0.0625$ , N = 400,  $J_0 = 0$ ,  $\kappa = 10^{20}$  ( $\Lambda \simeq 1$ ) and a triplet initial condition.

<sup>b</sup>Actual numerical results are listed first followed by the value obtained from the approximate formula, Eq. (37), in parentheses.

q is the same as that for  $\hat{\mathfrak{F}}^{*(2)}(\sigma)$ , i.e.,

$$\mathfrak{F}^{*(2)}(y_N) \approx \frac{\frac{1}{40} y_N^4 q^2}{1 + \frac{1}{40} y_N^4 q^2 / \mathfrak{F}'}$$
(40)

with

$$\mathfrak{F}' = \frac{q^{0.2} \ln(y_N)}{1 + q^{0.2} \ln(y_N)} \,. \tag{41}$$

The  $q^{1/2}$  dependence in three dimensions has been adequately explained in terms of the re-encounter mechanism, i.e., one knows that the first re-encounter probability in three dimensions goes asymptotically for large  $\tau$  (or small  $\sigma$ ) as  $\tau^{-3/2}$  which for small q yields the  $q^{1/2}$ result.<sup>1b,2,21</sup>

In an early attempt to extend this result to two dimensions, Deutch<sup>10</sup> found that the first re-encounter probability goes asymptotically for large  $\tau$  as  $\tau^{-1}(\ln\tau)^2$  and for small q this would yield a CIDNP dependence on q of  $[\ln(q^{-1/2})]^{-1}$ , which in the small q range is roughly

similar to the  $q^{0.2}$  that we estimate for small  $\sigma$  (but large q unless  $\sigma$  is very close to zero) in which case  $\hat{\mathfrak{F}}'$ is very close to unity anyway; in fact Deutch was analyzing what we have called the idealized model, for which it is incorrect to consider only the first re-encounter and for which rigorously  $\hat{\mathfrak{F}}^{(2)*} \rightarrow 1$ . On the other hand, for  $q/\sigma \leq 1$ , Eq. (37) shows a quadratic dependence upon q, which is known to be characteristic of the CIDNP effects due solely to the initial encounter<sup>2,22</sup> and therefore should not be dependent upon the dimensionality. Our result of Eq. (37) [or alternatively Eq. (40)] is therefore consistent with the model in which the effects of the initial encounter dominate for finite  $\sigma$  (or finite  $y_N$ ), while the re-encounter mechanism becomes relevant as  $\sigma = 0$ (or  $y_N \to \infty$ ), in which case  $\hat{\mathfrak{F}}^{(2)*}(\sigma)$  [or  $\mathfrak{F}^{(2)}(y_N)$ ] is already approaching its asymptotic value of unity. Typical differences between  $\hat{\mathfrak{F}}^{(2)*}(\sigma)$  and  $\hat{\mathfrak{F}}^{(3)*}(\sigma)$  are illustrated in Fig. 1, where for  $\sigma \gtrsim 1$  the two results are comparable, but they become markedly different for  $\sigma < 0.1$ .



FIG. 1.  $\mathfrak{F}^{(n)}(\sigma)$  versus  $\sigma$  for two-dimensional (n = 2) and three-dimensional (n = 3) diffusion. Results were obtained using the additional input N= 400,  $\Delta y = 1/16$ ,  $k = 10^{20}$  ( $\Lambda \simeq 1$ ),  $y_N = 25.9$ ,  $j_0 = 0$ , q= 0.064, and a triplet initial condition. The asymptotic  $(\sigma \rightarrow 0)$  results for the given input are  $\mathfrak{F}^{(2)} = 1$  and  $\mathfrak{F}^{(3)}$ 

TABLE	ш.	$\hat{\mathfrak{F}}^{*(2)}(\sigma)/\hat{\mathfrak{S}}$	$\widehat{\tau}^{*(2)}(\sigma, j_0 = 0).$
TABLE	ш.	\$*``)(σ)/§	$\mathfrak{F}^{*(2)}(\sigma, j_0 = 0).$

	$y_{ex} = 0.5^{b}$		y <sub>ex</sub> = 1		$y_{ex} = 2$	
$j_0/1.6$	$\sigma = 0.064$	0,64	0.064	0.64	0,064	0.64
10-1	1.0	1.0	1.0	1.0	1.0	1.0
1	0.97	0.99	0.91	0.97	0.76	0.90
10	0.59	0.63	0.53	0.47	0.48	0.33
10 <sup>2</sup>	0.53	0.40	0.50	0.34	0.41	0.20
$10^{3}$	0.51	0.36	0.45	0.25	0.33	0.10
10 <sup>4</sup>	0.49	0.31	0.41	0.18	0.27	0.055
10 <sup>5</sup>	0.46	0.26	0.37	0.13	0.22	0.029

<sup>a</sup>Finite difference results found using  $d^2/D^{(2)} = 1.6 \times 10^{-10}$  sec,  $\Delta y = 0.0625$ , q = 0.016, and a triplet initial condition. A

value of  $y_N = 26$  was used so the outer boundary would not influence the above results [cf. Eq. (27)] which then become  $\sigma$  dependent.

<sup>b</sup>Here we have introduced the dimensionless exchange distance  $y_{ex} = r_{ex}/d$ .

These features for two dimensions may be related to what we have called an "inward diffusion" effect in two dimensions, which is a purely geometric effect. That is, from Eq. (17), we have  $W_{j_i,j+1}^{(2)}/W_{j_i,j-1}^{(2)} = (1 + \Delta y/2y_j)/(1 - \Delta y/2y_j) > 1$ , while for three dimensions  $W_{j_i,j+1}^{(3)}/W_{j_i,j-1}^{(3)} = 1$ . Here we note that  $W_{ij}$  denotes the "transition probability" from the region of space surrounding the *j*th node to the space about the *i*th node. Thus for two dimensions the rate of "transition" from larger to smaller values of y is greater than the reverse rate, but it is equal in three dimensions. This argument reveals the finite difference basis for Eq. (2), such that  $\tau_1^{(2)} \rightarrow \infty$  as  $\mathcal{L}(\sigma) \rightarrow \infty$  due to a unit re-encounter probability.

Table III illustrates the effect of a finite exchange interaction on  $\hat{\mathfrak{F}}^{*(2)}(\sigma)$  for several values of  $\sigma$  and varying exchange interactions. Here it can be observed that the excluded volume<sup>2a</sup> effect due to a J(r) of large magnitude can be overcome by repeated radical collisions if a long enough time period (i.e., small  $\sigma$ ) is considered. The limit of  $\hat{\mathfrak{F}}^{*(2)}(\sigma \rightarrow 0)$  seen in Eq. (3) is then valid for any value of J(r), provided  $q \neq 0$ .

Our treatment so far has neglected any contributions from the  $T_{\star}$  states by analogy to the high field CIDN(E)P analysis for three dimensions. Such contributions are known to be important in low fields and we have recently shown them to be important for very viscous systems in three dimensions.<sup>5,23</sup> Since the nature of the CIDNP process in two dimensions seems to be significantly altered, one might question whether the  $T_{\star}$  states might not be of some importance for two dimensions. We have studied this problem by including all the triplet states in a two dimensional high-field analysis that is analogous to our recent three-dimensional study.<sup>5</sup> We could find no significant contributions from the  $T_{\star}$  states over the same range that gives negligible contributions for three dimensions. This implies that there is still rapid relative diffusion of the radicals through the region of space where the S and  $T_{\pm}$  levels may cross, <sup>24</sup> and one may neglect the  $T_+$  levels.

We shall see in Secs. VII and VIII that the forms given by Eqs. (32) and (37) and the interrelationships Eqs. (28)-(31) will be needed in actual experimental situations where source and sink terms are explicitly included. These terms will lead to a precise definition of time scales in experimental situations, and we shall see that quantities like  $\hat{\mathfrak{F}}^{(2)}(\sigma)$  are indeed needed but with a precise value of  $\sigma$  based upon the experimental time scale.

#### V. CIDEP ON A SURFACE

Many of the observations we have made with respect to CIDNP in two dimensions extend to the case of CIDEP.

We again note that certain expressions, which were found to be exact in three dimensions, carry over, when properly generalized, to two dimensions. They are

$$\hat{P}_{a}^{(2)}(\sigma, \mathrm{RI})/\hat{\mathcal{F}}^{(2)}(\sigma, \mathrm{RI}) = -\hat{P}_{a,k=0}^{(2)}(\sigma, S) = \hat{P}_{a,k=0}^{(2)}(\sigma, T_0)$$
(42)

which becomes, with the use of Eqs. (28)-(30),

$$\hat{P}_{a}^{(2)}(\sigma, \mathrm{RI}) = \frac{1}{2} \hat{\Lambda}^{(2)}(\sigma) \left[ 1 + \hat{\mathfrak{F}}^{(2)}(T_0, \sigma) \right] \hat{P}_{a, k=0}^{(2)}(\sigma, T_0) .$$
(43)

Also,

$$\hat{\mathcal{P}}_{a}^{(2)}(\sigma, T_{0}) = \left[1 + \hat{\mathcal{F}}^{(2)}(\sigma)\right] \times \left[1 + (1 - \hat{\Lambda}^{(2)}(\sigma) \hat{\mathcal{F}}^{(2)}(\sigma)\right]^{-1} \hat{\mathcal{P}}_{a, k=0}^{(2)}(\sigma, T_{0}), \quad (44)$$

and

$$\hat{\vec{P}}_{a}^{(2)}(\sigma, S) = [\hat{\Lambda}^{(2)}(\sigma) - 1] \hat{P}_{a}^{(2)}(\sigma, T_{0}) .$$
(45)

Thus all CIDEP polarizations may be obtained from  $\hat{P}_{a,k=0}^{(2)}(\sigma, T_0)$  [as well as  $\hat{\Lambda}^{(2)}(\sigma)$  and  $\hat{\mathfrak{F}}^{(2)*}(\sigma)$ ].

We first consider a "contact exchange" model in which exchange only occurs for radicals in contact (where  $\tau_I D/d^2 - \tau_I$ ).<sup>2a</sup> The results for this case may be reasonably well fit to the expression

$$\hat{P}_{a}^{(2)}(\sigma) \approx \left(\frac{\frac{5}{8}(q/\sigma)}{1+b\sigma^{-1}q^{6}}\right) \left(\frac{2j_{0}\tau_{I}}{1+\pounds(\sigma)(2j_{0}\tau_{I})^{2}}\right) , \qquad (46)$$

where

$$b \approx 5/2$$
,  $\epsilon \approx 1.2$  for  $|2j_0 \tau_f| \ll 1$ , and  $\sigma \gtrsim 0.1$ ;

 $b \approx 1$ ,  $\epsilon \approx 0.85$  for  $|2j_0 \tau_I| > 1$ , and/or  $\sigma \ll 1$ ,

and  $\tau_I$  is defined after Eq. (33). We show in Table IV a comparison between the results of Eq. (46) and the exact numerical results. When we compare Eq. (46) with the three-dimensional results,

$$P_a^{(3)}(\infty) \approx q^{1/2} \, \frac{2j_0 \, \tau_I}{1 + (2j_0 \, \tau_I)^2} \, \text{ for } q < 1 \, , \tag{47}$$

we see that in two dimensions the dependence on  $j_0 \tau_I$ is similar except for the term in  $\mathfrak{L}(\sigma)$  such that: (1) as  $\sigma \to 0$  and  $\mathfrak{L}(\sigma)$  goe logarithmically to infinity,  $\hat{P}_a^{(2)}(\sigma) \to 0$ which is consistent with Eq. (6) for the idealized model due to the predominance of the depolarizing mechanism and (2) as  $\sigma \to \infty$  so  $\mathfrak{L}(\sigma) \to 0$  and the importance of the  $(2j_0 \tau_I)^2$  term in the denominator is suppressed [i.e., in very short times the polarizing effects occur but there is insufficient time for the depolarizing effects due to spin exchange].

The linear q dependence in Eq. (46) is quite different from the  $q^{1/2}$  result for  $P_a^{(3)}(\infty)$ . We note that a linear q dependence is characteristic of an initial encounter mechanism<sup>1,2,22</sup> (which dominates in three dimensions

TABLE IV.  $\hat{P}_{a}^{(2)}(\sigma) \times 10^{3}$  from a contact exchange model.<sup>a</sup>

(Part I)		
q/1.6	$j_0 = 0.016^{b,c}$	1600. <sup>b,d</sup>
10-5	$2.1 \times 10^{-4} (2.1 \times 10^{-4})$	$0.77 \times 10^{-3} (1.1 \times 10^{-3})$
10~4	$2.1 \times 10^{-3} (2.1 \times 10^{-3})$	$0.77 \times 10^{-2} (1.1 \times 10^{-2})$
0.001	0.021(0.020)	0.077(0.106)
0.01	0.19(0.16)	0,73(0,77)
0.1	0.45(0.39)	2.9(2.6)
1.0	0,28(0,30)	4.5(4.7)
(Part II)		
$\sigma / 1.6$	$j_0 = 0.016^{c,e}$	1600. <sup>d,e</sup>
0.005	0.59(0.52)	1.2(1.3)
0.01	0.49(0.40)	1.2(1.2)
0.05	0.15(0.14)	0.65(0.70)
0.1	0.011(0.016)	0.19(0.18)
1.0	0.0045(0.0082)	0.13(0.11)

<sup>a</sup>Finite difference numerical results for  $\hat{\mathcal{P}}_{a}^{(2)}(\sigma) \times 10^{3}$  are listed first followed by the value obtained from Eq. (46) in parentheses. All results assume a contact exchange model using  $\tau_{1} \approx \Delta y/2 = 0.03125$ .

<sup>b</sup>Found using  $y_{ex} = 0$ ,  $\sigma = 0.064$ ,  $\Delta y = 0.0625$ ,  $y_N = 26$ .

<sup>e</sup>Here b = 5/2 and  $\epsilon = 1.2$  were used in Eq. (46).

<sup>d</sup>Here b = 1 and  $\epsilon = 0.85$  were used in Eq. (46).

•A value of q = 0.016 was employed to obtain these results.

only for  $\sigma < q/3$ ).<sup>2</sup> In two dimensions one also requires  $\sigma \ll q$  in order that Eq. (46) will show a weak dependence on q (e.g.,  $q^{0,2}$ ) which would resemble the logarithmic q dependence expected for re-encounters in two dimensions. [Because the value of  $\sigma$  affects both the q dependence as well as the  $j_0$  dependence we note that in Eq. (46) there is some ambiguity to assigning it properly.]

When we consider a finite range of exchange, the effects become more complex and are therefore less amenable to be fit by simple approximate forms. We therefore have separated the approximate forms to correspond to cases of small and large  $j_0$ . Thus, for the former we have

$$\hat{P}_{a}^{(2)}(\sigma) \approx \left(\frac{q/\sigma}{1+\frac{8}{3}q^{1,25}/\sigma}\right)(2j_{0}\tau_{\lambda})$$

$$|2j_{0}\tau_{\lambda}| \ll 1 \text{ and } \sigma \gtrsim 0.1 , \qquad (48)$$

where [cf. Eq. (5), recognizing the identification  $\tau_j - \tau_1(\lambda)$ ] we define

$$\tau_{\lambda} \equiv \tau_{1}(\lambda) D/d^{2} \simeq \frac{1}{\lambda d} \left( 1 + \frac{1}{2\lambda d} \right), \qquad (49)$$

with  $\lambda = 5 \ln 10/r_{ex} = 5 \ln 10/dy_{ex}$ .

This result is quite similar to that for contact exchange; the primary difference is the replacement of  $\tau_I$  by  $\tau_{\lambda}$  which represents the (dimensionless) lifetime of the exchanging radical pair in the region of finite extent in which the exchange interaction is appreciable. The generally good agreement between Eq. (48) and the exact numerical results is shown in Table V.

The results for large  $|j_0 \tau_{\lambda}|$  are characterized pri-



FIG. 2.  $\hat{P}_{a}^{(n)}(\sigma) \times 10^{3}$  versus  $\sigma$  for two- (n = 2) and three-dimensional (n = 3) diffusion. Additional input is N = 400,  $\Delta y = 1/16$ , k = 0, q = 0.064,  $j_0 = 1600.$ ,  $y_{ex} = 1$ ,  $y_N = 25.9$ , and triplet initial condition. The asymptotic  $(\sigma \rightarrow 0)$  results for the given input are  $\hat{P}_{a}^{(2)} = 0$  and  $\hat{P}_{a}^{(3)} \times 10^{3} = 25.5$ .

marily by their lack of any appreciable dependence upon  $j_0 \tau_{\lambda}$ . This is also characteristic of  $P_a^{(3)}(\infty)$  for which values asymptotic in  $j_0$  are obtained as  $j_0 \tau_{\lambda}$  becomes large. These asymptotic results are most easily expressed by the several forms

$$\hat{P}_{a}^{(2)}(\sigma) \approx \frac{q \tau_{\lambda}^{5}}{\sqrt{\sigma}} \text{ for } q/\sqrt{\sigma} < 1, \quad |j_{0} \tau_{\lambda}| \gg 1 ,$$
 (50)  
with

$$\delta \approx 1/2 \quad \text{for } \sigma \leq 0.1$$
$$\approx 0 \quad \text{for } \sigma > 0.1$$

and

$$\hat{P}_{a}^{(2)}(\sigma) \approx q^{\epsilon} \tau_{\lambda}^{\delta} / \mathcal{L}(\sigma) \quad q / \sqrt{\sigma} > 1, \quad \left| j_{0} \tau_{\lambda} \right| \gg 1 , \qquad (51)$$

with  $\epsilon \approx 0.1$  to 0.2 and  $\delta \approx 1$ . Table VI contains the ex-

TABLE V.  $\hat{P}_{a}^{(2)}(\sigma) \times 10^{3}$  for finite  $y_{ex}$  and  $|2j_{0}\tau_{\lambda}| \ll 1.^{a,b}$ 

(Part I) <sup>c</sup>		
q/1.6	$y_{ex} = 0.5$	1.0
10-5	$3.5 \times 10^{-4}$ (3.5 × 10 <sup>-4</sup> )	$6.5 \times 10^{-4} (7.3 \times 10^{-4})$
10-4	$3.5 \times 10^{-3}$ ( $3.5 \times 10^{-3}$ )	$6.5 \times 10^{-3}$ (7.2×10 <sup>-3</sup> )
0.001	0,035(0,035)	0.065(0.072)
0.01	0.32(0.29)	0.59(0.59)
0.1	0.76(0.68)	1.4(1.4)
1.0	0.46(0.47)	0.84(0.95)
(Part II) <sup>d</sup>		
$\sigma/1.6$	$y_{ex} = 0.5$	1.0
0.005	0.98(0.98)	1.8(2.0)
0.01	0.81(0.73)	1.5(1.5)
0.05	0.26(0.24)	0.48(0.49)
0,1	0.12(0.13)	0.23(0.26)
0.5	0.018(0.028)	0.033(0.057)
1.0	0.0075(0.014)	0.014(0.029)

<sup>a</sup>Actual numerical results found using  $y_N = 26$ ,  $\Delta y$ 

= 0.0625,  $j_0$  = 0.016, N = 400, and a triplet initial condition.

<sup>b</sup>The numerical result is listed first followed in parentheses by the value calculated from Eq. (48).

<sup>c</sup>A value of  $\sigma = 0.064$  was used in Part I.

<sup>d</sup>A value of q = 0.016 was used in Part II.

(P	art I) <sup>b</sup>						
		y <sub>ex</sub> =	1	y <sub>ex</sub> =	1.5	ye	<b>→x</b> = 2
q/2	1.6	$\sigma$ =0.0812	0.8	0.0812	0.8	0.0812	0.8
10	-5	0.0077	0.0023	0.010	0.0028	0.013	0.0028
10	-4	0.077	0.023	0.10	0.028	0.13	0.028
0.	. 001	0.77	0.23	1.0	0.28	1.3	0.28
0.	. 01	7.6	2.3	10.4	2.8	12.6	2.8
0.	. 1	41.6	22.9	61.6	27.9	81.3	28.0
(Part II	[)°						
		<i>q</i> =	= 0.016		<i>q</i> = 0.064		q = 0.16
$ au_{\lambda}$	$y_{ex}$	$j_0 = 1.6 \times 10$	$1.6 \times 10^{5}$	$1.6 \times$	$10^3$ 1.6×	×10 <sup>5</sup> 1.6	$3 \times 10^3$ 1.5 × 10 <sup>5</sup>
0.044	0.5	9.1	8.7	11.4	11.0	13.	.3 12.7
0.091	1.0	17.2	16.1	21.7	20.4	25.	1 23.4
0.139	1.5	24.6	22.9	31.1	29.2	35.	.7 33.2
0.189	2.0	31.4	29.2	39, 9	37.8	45.	.6 42.4

TABLE VI.  $\hat{P}_a^{(2)}(\sigma) \times 10^3$  for finite  $y_{ex}$  and  $|2j_0 \tau_{\lambda}| > 1.$ <sup>a</sup>

<sup>a</sup>Numerical results found using  $\Delta y = 0.0625$ .

<sup>b</sup>Results for  $q/\sqrt{\sigma} < 1$  found using  $j_0 = 1600$ .

act numerical results for  $\hat{P}_a^{(2)}(\sigma)$  which illustrate clearly the functional dependences seen in Eqs. (50) and (51). Note that Eq. (50) for shorter times is characterized by the linear dependence upon q for the initial encounter process, while Eq. (51) for longer times shows the weak dependence upon q that may be associated with re-encounters. In this latter case the main variation in  $\hat{P}_{a}^{(2)}(\sigma)$  is due to  $y_{ex}$ , the finite range of j(y), and to a lesser extent the logarithmic dependence upon  $\sigma$ . One sees that as  $\sigma \rightarrow 0$ ,  $\hat{P}_{\alpha}^{(2)}(\sigma)$  approaches zero as  $[\mathcal{L}(\sigma)]^{-1}$  consistent with the idealized model result of Eqs. (6) and (7). A comparison between  $\hat{P}_{a}^{(2)}(\sigma)$  and  $\hat{P}_{a}^{(3)}(\sigma)$  is shown in Fig. 2 for the case of  $|j_0 \tau_{\lambda}| \gg 1$ . It is seen how for  $\sigma \gtrsim 0.1$  they are both very similar, due to the initial encounter, but for  $\sigma < 0.1$  they deviate significantly. The importance of choosing the correct  $\sigma$  (or time scale) on the value of  $\hat{P}_a^{(2)}(\sigma)$  is clear from Fig. 2 as well as from Figs. 3 and 4, in which more extensive numerical results than those of Table VI are presented.



FIG. 3.  $\hat{P}_a^{(2)}(\sigma)$  versus  $\sigma$  for  $y_{ex} = 1$ . Results were found using also  $j_0 = 1600.$ ,  $\Delta y = 1/16$ , and either q = 0.16 (curve 1), q = 0.064 (curve 2), or q = 0.016 (curve 3).

<sup>c</sup>Results for  $g/\sqrt{\sigma} > 1$  found using  $\sigma = 0.008$ .

The results of this section [Eqs. (42)-(46) and (48)-(51)] will be seen to be important for the realistic situations discussed in Secs. VII and VIII, where the precise values of  $\sigma$  to be used will be clarified.

#### VI. HEISENBERG SPIN EXCHANGE

#### A. Idealized case

The result for Heisenberg spin exchange in the idealized case follows immediately from Eq. (5), so that for finite  $J_0$ ,  $\lim_{t\to\infty} |J_0 \tau_J(t)| = \infty$ . This means that the radical pair will continue to re-encounter until they have successfully randomized all spins and destroyed any polarization, provided only  $Q \ll J_0$  so there is no suppression of the exchange process.

#### B. Real cases

One may calculate the effects of spin exchange by selecting as the initial case  $P_a(t=0) = -1$  and with initial radial separation at  $r_I$  (or  $y_I = r_I/d$ ), i.e.,



FIG. 4.  $\hat{P}_{a}^{(2)}(\sigma)$  versus  $\sigma$  for  $y_{ex} = 2$ . Results were obtained using  $j_0 = 1600.$ ,  $\Delta y = 1/16$ , and either q = 0.16 (curve 1), q = 0.064 (curve 2), or q = 0.016 (curve 3).

TABLE VII.  $\Delta P^{(2)}(d_t, y_N)$ .<sup>a</sup>

(Part I	) Contact exchange model <sup>b</sup>	(Part 1 j <sub>0</sub> < j <sub>0</sub> (	II) For finite y <sub>ex</sub> , max) <sup>c</sup>
УN		УN	
26.0 19.7 13.4	0,298(0,298) 0,262(0,262) 0,213(0,213)	25.9 19.7 16.6 13.4 10.3 7.2	0.00094(0.00086) 0.00077(0.00072) 0.00070(0.00064) 0.00057(0.00055) 0.00045(0.00044) 0.00032(0.00032)
(Part I <i>yn</i>	II) For finite $y_{ex}$ , $j_0 > j_0 (max)^d$	(Part ) j <sub>0</sub> /1.6	IV) <sup>•</sup>
25.9 19.7 16.6 13.4 10.3 7.2	1.67(1.71) 1.78(1.84) 1.87(1.95) 2.01(2.11) 2.27(2.38) 2.95(2.93)	$10 \\ 10^{2} \\ 10^{3} \\ 10^{4} \\ 10^{5}$	$1.13(1.17) \\ 1.27(1.30) \\ 1.41(1.43) \\ 1.54(1.57) \\ 1.67(1.71)$

<sup>a</sup>The numerical result is presented first with the value calculated from the respective approximate formula from Sec. VI [Eqs. (55)-(57)] in parentheses.

<sup>b</sup>Results found using  $\Delta y = 0.0625$ , q = 0,  $j_0 = 3.2$ , and  $\tau_1 = 3.125 \times 10^{-2}$ .

°Results found using  $\Delta y = 0.0625$ ,  $y_{ex} = 2.9$ ,  $j_0 = 0.016$ , q = 0,  $r_I \gg d$ .

<sup>d</sup>Results found using  $\Delta y = 0.0625$ ,  $y_{ex} = 2.9$ , q = 0, and  $r_I \gg d$ ,  $j_0 = 1.6 \times 10^5$ .

<sup>e</sup>The  $j_0$  variation for the same case as Part III using  $y_N = 25.9$ ,  $y_{ex} = 2.9$ ,  $r_I \gg d$ ,  $\Delta y = 0.0625$ , and q = 0.

$$2 \operatorname{Re} \rho_{ST_0}(y_I, \tau = 0) = \delta(y - y_I) / y_I^2 , \qquad (52)$$

while  $\rho_{SS} = \rho_{T_0T_0} = \text{Im}\rho_{S,T_0} = 0$  for  $\tau = 0$ . Then  $\Delta P(y_I, \tau)$ , the change in polarization at time t after having started with the initial conditions expressed by Eq. (52), is given by<sup>2</sup>

$$\Delta P(y_I, \tau) = 1 - P_a(y_I, \tau) , \qquad (53)$$

or by the Laplace transform

$$\Delta \hat{P}(y_I, \sigma) = 1 - \hat{P}_a(y_I, \sigma) , \qquad (54)$$

with  $\hat{P}_a(y_I, \sigma)$  defined by Eq. (22). Equations (52)-(54) can refer to either two or three dimensions and results will be further qualified by the usual superscripts.

Our results for finite  $y_N$  and  $\sigma - 0$  are most readily fit by simple analytical forms which appear to be exact for contact exchange and nearly so for finite  $y_{ex}$ . Thus we have for contact exchange

$$\Delta P^{(2)}(d_t, y_N) = \frac{(\ln y_N)^2 (2j_0\tau_I)^2}{1 + 4(\ln y_N)^2 (j_0^2 + q^2) \tau_I^2}, \qquad (55)$$

where we have let  $r_I = d$ . The results for arbitrary  $r_I$  are readily obtained by use of the transfer factor of Eq. (35) in the usual way.<sup>2a</sup> The exact agreement of Eq. (55) with the computed results is illustrated in Table VII.

The results for finite  $y_{ex}$  are again best given separate ly for  $|2j_0 \tau_{\lambda}| \ll 1$  and  $\sigma \ge 1$  and for  $|j_0 \tau_{\lambda}| \gg 1$ . Thus we have

$$\Delta P^{(2)}(d_t, y_N) \approx (\ln y_N)^2 (2j_0 \tau_\lambda)^2 [1 - f(q)]$$
  
for  $|2j_0 \tau_\lambda| \ll 1$  and  $\sigma \ge 1$ , (56)

where  $f(q) \propto q^{1/3}$ , and is a small correction, and

$$\Delta P^{(2)}(d_t, y_N) \approx 1 + \frac{\frac{5}{2} \ln(1+j_0)}{(\ln y_N)^2 \lambda d} .$$
 (57)

The good agreement between Eqs. (56) and (57) and the computed results are illustrated in Table VII. One may obtain expressions for  $\Delta P^{(2)}(d_t, \sigma)$  by means of Eq. (27b) [cf. Ref. 2(b)].

One sees from both Eqs. (55) and (57) that in the limit  $y_N \rightarrow \infty$  the idealized result

$$\lim_{y_N \to \infty} \Delta P^{(2)}(d_t, y_N) = 1$$
(58)

is obtained provided  $q \ll j_0$ .

It is interesting to note that Eqs. (55)-(57) become the correct results for three dimensions if we let  $\ln y_N \rightarrow 1$ . In the case of Eq. (55), this has a simple interpretation and is seen by letting  $\tau_I^{(2)} = \tau_I \ln y_N$  [by analogy to our discussion of Eq. (34)], where again  $\tau_I^{(2)}$  is the effective lifetime of the interacting pair. Similarly, the form of Eq. (56) suggests that we may let  $\tau_{\lambda}^{(2)} = \tau_{\lambda} \ln y_N$ . The form of Eq. (57) showing the significant dependence upon  $y_{ex}$  (or  $\lambda^{-1}$ ) is not as transparent in the interpretation of the role of  $\ln y_N$ . The analysis as a function of  $\sigma$  similarly is characterized by a  $\tau_I^{(2)}(\sigma) = \tau_I \pounds(\sigma)$  and a  $\tau_{\lambda}^{(2)} = \tau_{\lambda} \pounds(\sigma)$ .

## VII. INITIAL POLARIZATION PROCESSES AND OBSERVABLES

We have seen in the previous sections how in two dimensions, unlike three dimensions, the relevant CIDN(E)P parameters do not achieve their asymptotic values after relatively short times (or large s) due to the additional logarithmic dependence on t. Thus, the two-time scale approach, which was found by Pedersen and Freed to be useful for 3D, is no longer applicable in the present case.

We now wish to consider how the results for  $\hat{\Lambda}(s)$ ,  $\hat{F}^*(s)$ ,  $\hat{P}_a(s)$  may be used to describe actual experimental situations. We start by introducing additional terms into the SLE given by Eq. (8). In order to adequately consider the time scales we need two types of terms: (1) radical initiation processes, and (2) radical and/or polarization termination reactions. In the former category we can consider such processes as photolytically created radical pairs or a process whereby a molecule reaches a catalytic site on the surface, at which point it may decompose into a radical pair. We shall simply represent such an initiation process by a quasi-firstorder process

$$\partial \rho_{\mathbf{p}} / \partial t = -k_0(t) \, \rho_{\mathbf{p}} \,, \tag{59}$$

where  $\rho_{p}$  is the density matrix of the diamagnetic precursor, and  $k_{0}(t)$  is the first order rate constant which may be time dependent (e.g., finite only while a light source is on) or time independent representing, for example, the rate at which the precursor reaches the surface. Since that radical pair will typically form at a particular interradical separation and in a particular spin state,

we must add to the right-hand side of Eq. (8) a term such as

 $+\hat{k}_{0}(r,t)[|T\rangle\rho_{b}\langle T|],$ 

where for definiteness we are assuming the radical pair forms in the pure triplet state. We also have

$$k_0(t) = \int_{d}^{\infty} \hat{k}_0(r, t) r^2 dr , \qquad (60)$$

with

$$\hat{k}_0(r,t) = k_0(t) \,\delta(r-r_I)/r_I^2 \quad \text{for } r_I \ge d \;. \tag{61}$$

We shall represent radical decay processes of type (2) (where  $k_1 = k_{1a} + k_{1b}$  the sum of the rates of radicals A and B, respectively) by a spin-independent first order decay rate:  $-k_1\rho$  (where  $k_1 = k_{1a} + k_{1b}$  the sum of the decay rates of radicals A and B, respectively) to be added to the right-hand side of Eq. (8). This decay could be due to a radical scavenging process and/or the rate of loss of radical from the surface and into one of the bulk phases. Also, we wish to include radical  $T_1$  and  $T_2$ processes which can destroy polarizations. We follow Freed and Pedersen in using a simple case, i.e., we let  $T_{1,a} = T_{1,b} = T_{2,a} = T_{2,b}$  and  $P_a^{\bullet q} = P_b^{\bullet q} \cong P^{\bullet q}(T = \infty)$ , so that the relaxation matrix **R** relevant for this problem is<sup>2,25</sup>

$$\left[\mathbf{R}(\rho - \rho_{eq})\right]_{ST_0} = -2T_1^{-1}\rho_{ST_0} , \qquad (62)$$

$$[\mathbf{R}(\rho - \rho_{\bullet \mathsf{q}})]_{SS} = [\mathbf{R}(\rho - \rho_{\bullet \mathsf{q}})]_{T_0 T_0} = -2T_1^{-1}(\rho_{T_0 T_0} - \frac{1}{4}) .$$
(63)

Thus, Eq. (8) becomes

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = -i\Im C^{\mathbf{x}}(\mathbf{r})\rho(\mathbf{r},t) + D\Gamma_{\mathbf{r}}\rho(\mathbf{r},t) + \mathbf{R}[\rho(\mathbf{r},t) - \rho_{eq}(\mathbf{r},t)] - k_{1}\rho(\mathbf{r},t) + \hat{k}_{0}(\mathbf{r},t)\rho_{p}(t)|T\rangle \langle T| + \kappa_{\mathbf{r}}\rho(\mathbf{r},t) .$$
(64)

With Laplace transform

$$[(s + k_1 + 2T_1^{-1}) + i\mathcal{H}^{\mathbf{r}}(\mathbf{r}) - D\Gamma_{\mathbf{r}} - \mathcal{K}_{\mathbf{r}}]\rho(\mathbf{r}, s)$$
$$= \rho(t = 0) + \hat{k}_0(r, s) * \rho_b(s) |T\rangle \langle T| + \mathbf{R} \rho_{eq}(\mathbf{r}, s) , \qquad (65)$$

where the asterisk implies a Laplace inverse convolution,  $^{\rm 26}$  and

$$s\rho_{\mathbf{b}}(s) = \rho_{\mathbf{b}}(0) - k_{0}(s) * \rho_{\mathbf{b}}(s)$$
 (66)

The time dependence of  $\rho_{oq}(\mathbf{r}, t)$ , the equilibrium density matrix, is due to the radical formative and decay processes while its r dependence is due to diffusion. That is, let us define

$$\sigma(\mathbf{r},t) \equiv \mathrm{Tr}\rho(\mathbf{r},t) = \mathrm{Tr}\rho_{\mathrm{eq}}(\mathbf{r},t) .$$
(67)

Thus  $\sigma(\mathbf{r}, t)$  gives the probability that the species of interest is a radical pair and separated by  $\mathbf{r}$  at time t. Then from Eqs. (64) and (13) we have

$$\frac{\partial \sigma(\mathbf{r}, t)}{\partial t} = D\Gamma_{\mathbf{r}} \sigma(\mathbf{r}, t) - k_1 \sigma(\mathbf{r}, t) + \hat{k}_0(\mathbf{r}, t) \rho_{\mathfrak{p}}(t) - k(\mathbf{r}) \rho_{ss}(\mathbf{r}, t) , \qquad (68)$$

and its Laplace transform is

$$[(s+k_1) - D\Gamma_{\mathbf{r}}]\sigma(\mathbf{r}, s)$$
  
=  $\sigma(t=0) + \hat{k}_0(\mathbf{r}, s) * \rho_{\mathbf{p}}(s) - k(\mathbf{r}) \rho_{ss}(\mathbf{r}, s)$ . (69)

Now the appropriate form of  $\rho_{eq}(\mathbf{r}, t)$  for Eqs. (64) [and (65)] is given by

$$\rho_{eq}(\mathbf{r},t) = \overline{\rho}_{eq} \,\sigma(\mathbf{r},t) \,, \tag{70}$$

$$\rho_{eq}(\mathbf{r},s) = \overline{\rho}_{eq} \sigma(\mathbf{r},s) , \qquad (71)$$

with

$$\overline{\rho}_{eq} \cong \frac{1}{N} \left( 1 - \hbar \mathcal{K} / k_B T \right) \tag{72}$$

in the high temperature approximation where N equals the number of spin eigenfunctions. [Equations (62) and (63) are based upon letting  $T \rightarrow \infty$  in Eq. (72).] Thus, Eqs. (68) and (69) may be transformed to equations in  $\rho_{eq}$  by multiplying through by  $\overline{\rho}_{eq}$ .

We shall now assume that at t=0,  $\rho_{p}(0)=1$  while  $\rho(0)=\sigma(0)=0$ . Then we may rewrite Eq. (65) as

$$[(s + k_1 + 2T_1^{-1}) + i\mathcal{K}^{s}(\mathbf{r}) - D\Gamma_{\mathbf{r}} + k(r)(|S\rangle \langle S|) P_S + B(\mathbf{r}, s) P_S]\rho(\mathbf{r}, s) = \hat{k}_0(\mathbf{r}, s) * \rho_{\mathbf{s}}(s) |T\rangle \langle T| + A(\mathbf{r}, s) , \qquad (73)$$

where  $P_s$  is a projection operator on  $\rho(\mathbf{r}, s)$  such that  $P_s \rho(\mathbf{r}, s) = \rho_{ss}(\mathbf{r}, s)$  and

$$A(\mathbf{r}, s)$$

$$=\frac{1}{2T_{1}}\left(\frac{1}{s+k_{1}-D\Gamma_{r}}\right)\left(\hat{k}_{0}(r,s)*\rho_{p}(s)\right)\left(\left|S\right\rangle\left\langle S\right|+\left|T_{0}\right\rangle\left\langle T_{0}\right|\right)$$
(74)

and

$$B(\mathbf{r}, s) = \frac{1}{2T_{1}} \left( \frac{1}{s + k_{1} - D\Gamma_{\mathbf{r}}} \right) k(\mathbf{r}) \left( \left| s \right\rangle \left\langle s \right| + \left| T_{0} \right\rangle \left\langle T_{0} \right| \right) \right).$$
(75)

The first term on the right hand side of Eq. (73) is the normal source term, while A(r, s) is an "effective" source term arising from radical pairs first generated in the triplet state at  $r_I$ , then being relaxed by  $T_1 = T_2$  processes to the random state while diffusing away from  $r_I$ . In dimensionless units this additional source term is of order  $(T_1^{-1}d^2/D)/(\sigma + k_1d^2/D - \Gamma_{\tau})^{-1}$  compared to the normal source term. As long as  $T_1^{-1}d^2/D$  is small compared to unity (note that for  $D \sim 10^{-5}$  cm<sup>2</sup>/sec,  $d \sim 4 \times 10^{-8}$  sec,  $T_1 \sim 10^{-6}$  sec, it is ~  $1.6 \times 10^{-4}$ ) then we would expect radicals to have diffused away a significant distance before they relax, so this "source" of radicals (requiring re-encounters) should be small compared to the primary source term, and we shall neglect it in our further discussion.<sup>27</sup>

The term B(r, s) on the left-hand side is an effective recombination process added to the primary recombination process, which arises from the way in which  $\rho_{eq}$  is affected by the recombination process. This additional term is again of order  $(T_1^{-1}d^2/D)/(\sigma+k_1d^2/D-\Gamma_{\bar{r}})^{-1}$  compared to the primary recombination term, and we shall also neglect it for reasons similar to those given.

The resulting Eq. (73) is then equivalent to the Laplace transform of Eq. (8) provided only in the latter  $s - s + k_1$  $+2T_1^{-1} = s'$ , and  $\rho(0)$  is replaced by  $\hat{k}_0(\mathbf{r}, s) * \rho_p(s) | T \rangle \langle T |$ (or any other choice of initial spin state). Suppose, now, the initiation process is a constant light source turned on at t = 0 so  $k_0(t) = k_0 U(0)$  where U is the unit step function. Then  $\rho_p(s) = [s + k_0]^{-1}$  while  $k_0(s) * \rho_p(s) = [s + k_0]^{-1}$ . [We would get the same result for a surface-catalyzed

process with constant  $k_0$  provided we could choose a w t=0 such that  $\rho_p(t=0)=1$ .] Also, the important CIDN(E)P  $\hat{P}$ terms given in Eqs. (21)-(25) are determined from th

 $\sigma_{\mathcal{D}}(y,\sigma)$ . Thus in the present case we have

$$\overline{\rho}(y,\sigma) \cong \frac{\kappa_0}{\sigma + \kappa_0} \rho(y,\sigma + \kappa_1 + 2d^2/T_1D,T)$$
(76)

where  $\rho$  on the RHS is for triplet initial formed at  $y_I$  as calculated in the previous sections with  $\kappa_0 \equiv k_0 d^2/D$  and  $\kappa_1 \equiv k_1 d^2/D$ , while  $\overline{\rho}(y, \sigma)$  is the density matrix based upon Eq. (73). Now for 3D one usually solves for, e.g.,  $\lim_{\sigma \to 0} \hat{\sigma}(\sigma) = \lim_{t \to \infty} \mathcal{P}(t)$ . In the present case we shall assume  $\kappa_0$  is very small, so that there is negligible depletion of species relative to other processes. Thus it is meaningful to take the limit  $\sigma = 0$  but with  $\sigma \gg \kappa_0$ . [In the true limit of  $(\sigma \to 0) < \kappa_0$ ,  $\rho_p \to 0$ , and no new radicals forms, while the original radical has either reacted or relaxed its polarization.<sup>27</sup>] This is,

$$\lim_{\sigma \to 0} \overline{\sigma\rho}(y,\sigma) \cong \kappa_0 \ \rho(y,\kappa_1 + 2d^2/T_1D,T) , \qquad (77)$$

and it follows that, e.g.,

$$\lim_{\substack{\tau \to \infty \\ \kappa_0^{-1}}} \overline{\varphi}(\tau) \cong \left(\frac{\kappa_0}{\kappa_1 + 2d^2/T_1 D}\right) \widehat{\varphi}(\sigma = \kappa_1 + 2d^2/T_1 D) , \qquad (78)$$

which is a well-defined quantity with  $\hat{\sigma}(\sigma) = 1 - \hat{\mathcal{F}}(\sigma)$  given, for example, by Eq. (37). The actual time evolution of  $\sigma(\tau)$  is given by the Laplace inverse transform of

$$\frac{\kappa_0}{\sigma + \kappa_0} \left[ \frac{\hat{\varphi}(\sigma + \kappa_1 + 2d^2/T_1D)}{\sigma + \kappa_1 + 2d^2/T_1D} \right] \equiv \widetilde{\varphi}(\sigma) , \qquad (79)$$

for which the formulas of Sec. IV may be used for  $\hat{\phi}(\sigma)$ .

It immediately follows from the relation  $\mathfrak{F}(t) = 1 - \mathfrak{O}(t)$  that we can obtain  $\overline{\mathfrak{F}}^{*(2)}(\infty)$  from Eq. (78) while  $\overline{\mathfrak{F}}(\sigma) = (1/\sigma) - \overline{\mathfrak{O}}(\sigma)$  and Eq. (79) may used for  $\overline{\mathfrak{O}}(\sigma)$ . Thus, for example, we get using Eqs. (37) and (79)

$$\hat{\mathfrak{F}}^{*(2)}(\infty) \cong 1 - \left(\frac{\kappa_0}{\kappa_1'}\right) \frac{1}{1 + \frac{1}{2} q^2 / (\kappa_1^{1,7} \hat{\mathfrak{F}}')} , \qquad (80)$$

with

$$\hat{\mathbf{f}}' = \frac{\mathfrak{L}(\kappa_1') q^{0.2}}{1 + \mathfrak{L}(\kappa_1') q^{0.2}}$$
(81)

and with  $\kappa_1' \equiv \kappa_1 + 2d^2/T_1D$ .

One may calculate  $P_a(\infty)$  [and  $\hat{P}_a(t)$ ] merely by replacing  $\mathcal{P}$  by  $P_a$  in Eqs. (78) and (79) [compare Eqs. (21) and (22)]. Thus, for example, from Eq. (46) we get

$$P_{a}^{(2)}(\infty) \cong \left(\frac{\kappa_{0}}{\kappa_{1}'}\right) \frac{\frac{5}{6} (q/\kappa_{1}')}{1 + bq^{\epsilon}/\kappa_{1}'} \left(\frac{2j_{0} \tau_{I}}{1 + \mathfrak{L}(\kappa') (2j_{0} \tau_{I})^{2}}\right) .$$
(82)

Thus we see in all these examples that the term  $\pounds(\sigma)$ +  $-\frac{1}{2}\ln\sigma$  as  $\sigma \rightarrow 0$  will now have the finite value  $-\frac{1}{2}\ln\kappa'_1$ which is not very sensitive to the actual value of  $\kappa'_1$ . Equation (82) may be compared with previous results on steady-state polarizations in three dimensions. In particular (when we ignore finite  $P_{eq}$  as we have above for simplicity), then it was found for 3D from the two-time scale approach that the observed intensity for the present model is just

$$I_{a}^{(3)\,ss} = \frac{k_{0,a}\,T_{1,a}}{k_{1,a}\,T_{1,a}+1}\,P_{a}^{(3)}(\infty)\,, \tag{83}$$

which is very similar in form to Eq. (78) except that  $\hat{P}_{a}^{(2)}(\kappa_{1}+2d^{2}/T_{1}D)$  replaces  $P_{a}^{(3)}(\infty)$ . This, then, clarifies the way in which the present  $\sigma$ -dependent results may be used to predict steady-state polarizations, for example.

Another way of obtaining an expression like Eq. (78) but for  $P_a^{(2)}(\infty)$  is to express the z component of magnetization due to the CIDEP by

$$M_{aa}(t) = M_{aa}(0) + \int_0^t \exp\left[-k_1(t-t')\right] P_a(t-t') k_0(t') dt' \quad (84)$$

That is, we assume the radical-generating mechanism is turned on at t=0, the amount of radical formation for the time between t' and t'+dt' is  $k_0(t')dt'$ ; while  $P_a(t-t')$ gives the polarization generated at t from a unit probability of radical pair at time t', and  $\exp[-k_1(t-t')]$  gives the fractional probability that a radical pair which exists at time t' will not yet be scavenged at time t. [The full  $T_1$ ,  $T_2$  problem, as we have already seen, is more complex and we do not consider it here other than to note that by analogy with the simplest version yielding Eqs. (76)-(82) we may let  $k_1 - k_1 + 2/T_1$ .]

The Laplace transform of Eq. (84) is then

$$M_{sa}(s) - \frac{1}{s} M_{sa}(0) = P_a(s+k_1) k_0(s) , \qquad (85)$$

and if  $k_0(t')$  is taken as the unit step function at t=0 (i.e., no appreciable depletion of precursor) we obtain

$$sM_{aa}(s) = k_0 P_a(s+k_1) = k_0 \frac{\hat{P}_a(s+k_1)}{(s+k_1)}$$
, (86)

where we have set  $M_{sc}(0) = 0$  [which is of the same form as Eq. (79) with  $\sigma > \kappa_0$  as is being assumed here]. Then, we have

$$\lim_{s \to 0} s M_{sa}(s) = k_0 P_a(k_1) = \frac{k_0}{k_1} \hat{P}_a(k_1) , \qquad (87)$$

which is of the same form as Eq. (78).

In previous work on 3D, it was shown that a two-time scale approach could be used to generate rate equations with time-independent rate coefficients. In order to illustrate the generalization required in the present work we differentiate Eq. (84) with  $k_1 = 0$  to obtain

$$dM_{za}(t)/dt = \int_{0^{-}}^{t} P_{a,b}(t-t') k_0(t') dt' , \qquad (88)$$

where  $P_{a,b}(t) \equiv \partial P_a(t)/\partial t$  and we have taken  $P_a(t=0)=0$  to obtain Eq. (88); i.e., there is a time lapse (which need only be infinitesimal) between radical-pair formation and the development of polarization. This is physically reasonable (since it is nothing more than a statement of causality) and it is also consistent with our results on  $P_a(t)$  in Sec. V.

We also note that Eq. (88) when Laplace transformed just yields Eq. (85) with  $k_1 = 0$  as it should. When  $k_1 \neq 0$ , we replace  $P_{a,b}(t-t')$  in Eq. (88) by  $\exp[-k_1(t-t')] \times [P_{a,b}(t-t') - k_1 P_a(t-t')]$ , and the Laplace transform is just Eq. (85).

Equation (88) is also consistent with general properties of response functions.<sup>28</sup> We can regard  $P_{a,b}(t)$  as the polarization at time t resulting from a delta function input pulse at t=0. Then  $dM_{ga}(t)/dt$  is the observed rate for an input rate of  $k_{0,a}(t)$ . The expression  $P_{a,b}(t) = dP_a(t)/dt$  is indeed the relation between the response to a delta function and the response to a unit step function at t = 0.<sup>28</sup> In the 3D theory, we regarded  $P_a(t)$  as going very rapidly from zero to its asymptotic value  $P_a^{\infty}$  as soon as the radical pair is formed. In this case  $P_a(t) + P_a^{\infty} U(t)$  where U(t) is the unit step function. Then  $P_{a,b}^{\infty}(t)$  $= P_a^{\infty} \delta(t)$  and from Eq. (76)  $[dM_{sa}(t)/dt]_{b0} = P_a^{\infty} k_{0,a}(t)$  as it should. [More precisely we should use  $U(t + \epsilon)$  and  $\delta(t + \epsilon)$  where  $\epsilon$  is an infinitesimal time delay in order to be consistent with our above choice of  $P_a(t=0)=0$ .] This point of view will be adopted in our discussion of bimolecular encounters.

### VIII. RANDOM BIMOLECULAR COLLISIONS AND OBSERVABLES

We now consider the problem of bimolecular collisions in 2D, although it is useful to keep the conventional 3D theory in mind. The usual basis of the 3D theory is the Smoluchowski solution for the coagulation model.<sup>17,29</sup> One solves the diffusion equation for B particles at their initial concentration (say, at unit concentration) relative to an A molecule on which B particles coalesce. This solution may be interpreted to yield the rate of first bimolecular encounter of A with a B molecule or  $\Phi(t)$ , but it does so by treating the effect of each B molecule as being independent (cf. Collins and Kimball, Ref. 19). (In effect, one is solving for the interaction between a single A and a single B molecule, where the concentration of B is just 1/V with V the volume of the sample.) One then obtains in 3D

$$\Phi(t) = 4\pi D d \left( 1 + \frac{d}{\sqrt{\pi D t}} \right) n_{\mathrm{B},0} , \qquad (89)$$

where  $n_{B,0}$  is the initial uniform concentration of B (and we could let  $n_{B,0} \equiv 1$ ).  $\Phi(t)$  represents the flux of B particles (with radius d/2) into a sphere of radius d/2 about the point center of an A particle. This flux is time varying only for short times and soon assumes its steady state value. The boundary condition at r = d for t > 0 is  $n_B(r, t)$ = 0, an absorbing wall. [The discontinuity in Eq. (89) for t = 0 may be attributed to the immediate absorbing of any B molecule initially at r = d. We neglect this by only considering t > 0.] For times  $t \gg d^2/D$  the transient term in Eq. (89) is unimportant, and one usually uses the steady state form

$$2k_2 = 4\pi Dd , \qquad (90)$$

where  $2k_2$  is the rate constant for new bimolecular encounters at a particular center separation of d. In the case of 2D, the equivalent treatment yields

$$\Phi(t) = (16D/\pi) I(0, 1, Dt/d^2) n_{\rm B,0} , \qquad (91)$$

where  $I(0, 1, Dt/d^2)$  is an integral over Bessel functions discussed elsewhere<sup>30</sup> (or alternatively it could be calculated by our present methods by starting with a uniform initial distribution of B). This expression never reaches a steady-state value since it is easy to show that an infinite outer concentration would be needed to support the steady state.<sup>31</sup> In fact it goes asymptotically with t as  $\Phi(t) = [8\pi D/\ln(4Dt/d^2)]n_{B,0}$ . The physical reason for the difference between 2 and 3D may again be attributed to the re-encounter probability  $t_f(r) = d/r$  in 3D and unity in 2D. Thus, in 2D, as time progresses, one must ultimately "coagulate" all B molecules, so  $\Phi(t)$ must go to zero. In 3D, since  $t_f(r) < 1$ , a uniform initial distribution of B molecules can never be fully depleted.

Now, in the context of our earlier discussion,  $\Phi(t)$ for  $n_{B,0} = 1$  [which shall hereafter be referred to as  $\Phi_0(t)$ ] can be regarded as the rate of first bimolecular encounter per A molecule at time t due to a unit concentration of B molecules at time t=0. Thus, the general expression for the number of first bimolecular encounters at time t per A molecule is the integral

$$N(t) = \int_0^t \Phi_0(t - t') n_{\rm B}(t') dt'$$
(92)

having a Laplace transform<sup>32</sup>

$$N(s) = \Phi_0(s) n_{\rm B}(s) . \tag{93}$$

The lower limit in Eq. (92) reflects the choice of t=0, as the time when  $n_{\rm B}=n_{\rm B,0}$ , e.g., radicals B have just been created, or else their concentration has remained constant up to t=0 because of absence of radicals A and/ or scavengers for t<0 and the upper limit the fact that we want  $\Phi(t)$  only for t>0. Equation (92) allows for a time varying spatially uniform concentration of  $n_{\rm B}$ . Then the overall rate is obtained by differentiating Eq. (92) to obtain

$$\frac{dN(t)}{dt} = \int_0^t \Phi_{0,\delta}(t-t') n_{\rm B}(t') dt' + \Phi_0(O_{\star}) n_{\rm B}(t) , \qquad (94)$$

where  $\Phi_{0,\delta}(t) \equiv d\Phi_0(t)/dt$ . [This yields the same Laplace transformed expressions as Eq. (92).] In the special case where  $\Phi_0(t)$  is constant [e.g., Eq. (89) neglecting the transient term which is unimportant for long times anyway], one has  $\Phi_{0,\delta}(t) \equiv 0$  and  $dN(t)/dt \equiv \Phi_0 n_{\rm B}(t)$ , or the usual result used for diffusion-controlled reactions. When the small transient term is included, but one recognizes that  $\Phi_{0,\delta}(t)$  is very small, except for  $t \approx 0$ , and assume  $n_{\rm B}(t)$  is a slower varying function of t, one can write the approximate form

$$\frac{dN(t)}{dt} \approx 4\pi D d n_{\rm B}(t) \left(1 + \frac{d}{\sqrt{\pi dt}}\right) \text{ for } t > 0 \text{ in } 3D . \tag{95}$$

In the case of 2D,  $\Phi_0(t)$  is always a function of t, so the equation (94) must always be used with  $\Phi_0(O_*) = 4\pi D/(\pi D O_*/\rho)^{1/2}$ , where this term will cancel an equivalent term in the integral. That is, using the expansion of  $\Phi_0(t) = 4\pi D x \left\{ (\pi \alpha)^{-1/2} + \frac{1}{2} - \frac{1}{4} (\alpha/\pi)^{1/2} + \frac{1}{8} \alpha - \cdots \right\}$  with  $\alpha = Dt/d^2$ , one has

$$\frac{dN}{dt} \approx 4\pi Dd \left[ n_{\rm B}(t) \left( \frac{1}{2} + \frac{d}{\sqrt{\pi Dt}} \right) + \int_0^t \left( -\frac{1}{8} \frac{1}{(\alpha' \pi)^{1/2}} + \frac{1}{8} - \cdots \right) n_{\rm B}(t') dt' \right] , \quad (96)$$

with  $\alpha' = D(t-t')/d^2$ , where we have used the same approximation as in Eq. (95).

Now the above discussion is for a single A molecule. In particular, Collins and Kimball<sup>19</sup> point out that the usual derivation should be associated with the *a priori* probability at t = 0 that the A particle will react at a later time. That is, the A particle is known to exist initially.

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Then the overall rate would depend upon  $n_{A,0}$ . Thus we would obtain the total number of first encounters from A and B molecules per unit volume by rewriting Eq. (92) as

$$N_{\rm A}(t) = \int_0^t \Phi_0(t - t') n_{\rm A}(t') n_{\rm B}(t') dt' , \qquad (97)$$

so Eq. (94) becomes

$$\dot{N}_{\rm A}(t) = \frac{dN_{\rm A}(t)}{dt} = \int_0^t \tilde{\Phi}_{0,0} (t - t') n_{\rm A}(t') n_{\rm B}(t') dt' , \qquad (98)$$

with  $\tilde{\Phi}_{0,\delta}(t-t') \equiv \Phi_{0,\delta}(t-t') + \delta(t-t') \Phi_0(O_*)$  which yields the usual form for constant  $\Phi_0$ 

$$\dot{N}_{A}(t) \equiv \frac{dN_{A}(t)}{dt} = \Phi_{0} n_{A}(t) n_{B}(t) .$$
(99)

Using CIDN(E)P formalism,  ${}^2 \mathfrak{F}(X, t)$  is the probability of a spin-selective reaction for a radical pair initially in contact and with spin state  $X = T_0$ , S, or RI. Thus, by analogy to Eqs. (84) and (88), wherein we regard  $\mathfrak{F}(X, t)$ as the molecular response to the first encounter of the radical pair, we have

$$-\frac{dn_{\mathbf{A}}(t)}{dt} = \int_{0}^{t} \mathfrak{F}_{\delta}(X, t-t') \, \dot{N}_{\mathbf{A}}(\tau) \, d\tau = \int_{0}^{t} dt' \, \mathfrak{F}_{\delta}(X, t-t') \\ \times \int_{0}^{t'} \tilde{\Phi}_{0,\delta}(t'-t'+\epsilon) \, n_{\mathbf{A}}(t'') \, n_{\mathbf{B}}(t'') \, dt'' \, , \qquad (100)$$

where  $\mathfrak{F}_{\delta}(X, t) \equiv \mathfrak{dF}(X, t)/\mathfrak{d}t$ . In the 3D case where  $\Phi_{0,\delta} = 0$  and  $\mathfrak{F}_{\delta}(t) \cong \mathfrak{F}(\infty) U(t)$  one recovers the simple form

$$-\frac{dn_{\mathbf{A}}(t)}{dt} = \mathfrak{F}(\infty) \Phi_0 n_{\mathbf{A}}(t) n_{\mathbf{B}}(t) , \qquad (101)$$

but the more general form of Eq. (100) is needed for 2D. The Laplace transform of Eq. (100) is

$$s n_{\mathbf{A}}(s) - n_{\mathbf{A}}(t=0) = -\widehat{\mathfrak{F}}(X,s) \widehat{\Phi}_{0}(s) \overline{n_{\mathbf{A}} n_{\mathbf{B}}(s)} , \qquad (102)$$

where

$$\overline{n_{\rm A} n_{\rm B}(s)} \equiv \int_0^\infty n_{\rm A}(t) n_{\rm B}(t) dt , \qquad (103)$$

and we have used the fact that the Laplace transform of  $\mathfrak{F}^{(2)}_{\theta}(X,\tau)$  is

$$\int_{0}^{\infty} e^{-\sigma\tau} \mathfrak{F}_{\delta}^{(2)}(X,\tau) d\tau = \hat{\mathfrak{F}}^{(2)}(X,\sigma) - \mathfrak{F}^{(2)}(X,\tau=0) = \hat{\mathfrak{F}}^{(2)}(X,\sigma) ,$$
(104)

etc. [see Eqs. (21)-(25) and Footnote 2(a)].

By similar arguments we obtain for the magnetization

$$dM_{a}^{a}(t)/dt = \int_{0}^{t} P_{a,b}(\mathbf{RI}, t-t') \dot{N}_{a}(t') dt'$$
(105)

when we neglect any initial polarization at the time of a new encounter.<sup>2</sup> One can now use Eq. (98) for  $\dot{N}_a(t')$  in Eq. (105) in order to obtain a complete expression. The final analysis of Eq. (105) is also best handled by Laplace transforming the multiple convolution. Then, in this case of CIDEP in the presence of a chemical reaction one may use Eq. (42) in the form  $\hat{P}_a^{(2)}(\sigma, \text{RI}) = \hat{P}_{a,k=0}^{(2)}(\sigma, T_0) \hat{\mathcal{F}}^{(2)}(\sigma, \text{RI})$  in the Laplace transform of Eq. (105), where both  $\hat{P}_{a,k=0}^{(2)}(\sigma, \text{RI})$  are given in the previous sections. [Note that the Laplace transform in our notation of  $P_{a,k}^{(2)}(\tau, \text{RI})$  is  $\hat{P}_a^{(2)}(\sigma, \text{RI})$ , cf. Eq. (104).] We now wish to consider the situation where there is a radical scavenging reaction (or else  $T_1$  processes). We shall consider as our example the rate of production of recombination product R(t). We may, utilizing Eq. (100), express it as

$$\frac{dR(t)}{dt} = \int_0^t dt' \left[ \exp(-k_1(t-t')) \mathfrak{F}_{\mathfrak{s}}(t-t') \right] \\ \times \int_0^{t'} \left[ \exp(-k_1(t-t')) \tilde{\Phi}_{0,\mathfrak{s}}(t'-t''+\epsilon) n_{\mathfrak{A}}(t'') n_{\mathfrak{B}}(t'') dt'' \right]$$
(106)

where  $\exp[-k_1(t-t'')]$  represents the probability of survival from scavenging (or leaving the surface) at time t', given that radicals have been formed at t'' (e.g., by a sudden burst of radiation at time  $t \approx 0$ ) and we have set R(t=0)=0. That is, the rate of first encounter at t',  $\Phi_{0,\delta}(t'-t'')$  is reduced by this probability of surviving the scavenging reaction prior to the encounter. Also, once they have encountered, the rate of formation of recombination product,  $\mathfrak{F}_{\delta}(t-t')$  is reduced by  $\exp[-k_1(t-t')]$ or the probability of survival during the multiple re-encounter process. (We are, of course, assuming that the scavenging and recombination reactions are statistically independent.)

Now we consider the rate of loss of radicals A, which is equal to

$$-\frac{dn_a(t)}{dt} = \frac{dR(t)}{dt} + k_{1,a} n_a(t) .$$
 (107)

The Laplace transforms of Eqs. (106) and (107) are obtained with the aid of Eq. (102):

$$sR(s) = \hat{\mathfrak{F}}(s+k_1)\,\tilde{\Phi}_0(s+k_1)\,n_{\rm A}\,n_{\rm B}(s)\,, \qquad (108)$$

with R(t=0)=0 and

$$sn_{\rm A}(s) - n_{\rm A}(0) = -sR(s) - k_{1,a}n_{\rm A}(s)$$
 (109)

If, for simplicity, we assume B is in excess and  $k_{1,b} \approx 0$ , so  $n_{\rm B}$  is approximately constant at  $n_{\rm B,0}$  and  $k_1 \approx k_{1,a}$ , then we have  $n_{\rm A}n_{\rm B}(s) = n_{\rm A}(s)n_{\rm B,0}$  and Eqs. (108) and (109) become

$$sR(s) = \hat{\mathfrak{F}}(s + k_{1,a}) \hat{\Phi}_0(s + k_{1,a}) n_{\mathsf{A}}(s) n_{\mathsf{B},0}$$
(110)

and

$$n_{\mathbf{A}}(s) = n_{\mathbf{A}}(0) / \left[ s + k_{1,a} + \hat{\mathfrak{F}}(s + k_{1,a}) \, \hat{\Phi}_{0}(s + k_{1,a}) \, n_{\mathbf{B},0} \right] \,. \tag{111}$$

Then

$$\lim_{t \to \infty} R(t) = \frac{\hat{\mathfrak{F}}(k_{1,a})\hat{\Phi}_0(k_{1,a})n_{\mathsf{A}}(0)n_{\mathsf{B},0}}{k_{1,a} + \hat{\mathfrak{F}}(k_{1,a})\hat{\Phi}_0(k_{1,a})n_{\mathsf{B},0}}, \qquad (112)$$

which becomes the usual 3D result by making the replacements  $\hat{\mathfrak{F}}^{(2)}(k_{1,a}) \rightarrow \hat{\mathfrak{F}}^{(3)}(t=\infty)$ ;  $\hat{\Phi}_0^{(2)}(k_{1,a}) \rightarrow \hat{\Phi}_0^{(3)}$ . Thus we obtain a well-defined limiting recombination concentration  $R(t \rightarrow \infty)$ . On the other hand  $\lim_{t\rightarrow\infty} n_A(t) = 0$  in both 2D and 3D as it must. The complete time evolution R(t)[or  $n_A(t)$ ] would follow from Laplace inverting Eqs. (110) and (111) utilizing the appropriate forms for  $\hat{\mathfrak{F}}(s)$  (and  $\hat{\Phi}_0(s)$ ) from Sec. IV. The manner in which CIDNP polarizations may be obtained from R(t) is discussed by Freed and Pedersen.<sup>33</sup>

One can, of course, further generalize this approach to explicitly include the process(es) by which radical pairs first appear on the surface as was done in Sec. VII, but this is a straightforward generalization of the methods already outlined in these two sections.

Also, we note that since  $\Lambda(t) = \mathfrak{F}_0(S, t)$  or  $\hat{\Lambda}(s) = \hat{\mathfrak{F}}_0(S, s)$  the results we have obtained above for  $\hat{\mathfrak{F}}(\sigma)$  may also be used for  $\hat{\Lambda}(\sigma)$ , which may then be compared to the usual spin-independent theories of reaction kinetics.

In the case of Heisenberg spin exchange we are again interested in the rate of first bimolecular encounter per A molecule, but we neglect any reactions. Thus, this rate is given by

$$\overline{N} = \Phi_0(t) n_{\rm B} , \qquad (113)$$

where  $n_{\rm B}$  is constant after B has been produced or has appeared on the surface. Then we can write [by analogy to Eq. (88)]

$$\dot{M}_{aa}(t) = \int_0^t P_{a,b}(\text{HE}, t - t') \, \dot{\bar{N}}(t') \, d\tau + P_a(\text{HE}, t = 0) \, \dot{\bar{N}}(t) ,$$
(114)

where, in the present case,  $P_a(t=0) = -1$ , and  $P_a(\text{HE}, t)$  is given in terms of  $\Delta P(t)$  by Eq. (53) or

$$\hat{M}_{aa}(\sigma) - M_{aa}(0) = \sigma^{-1} \hat{P}_a(\text{HE}, \sigma) \hat{\Phi}_0(\sigma) n_{\text{B}} .$$
(115)

Then by analogy to the 3D case<sup>2</sup> we can write

$$\hat{\omega}_{\rm HE}(\sigma) \equiv \Delta \hat{P}(d_t, \sigma) \,\hat{\Phi}_0(\sigma) \, n_{\rm B} \,, \tag{116}$$

where  $\hat{\omega}_{\text{HE}}(\sigma)$  is the ( $\sigma$ -dependent) Heisenberg exchange frequency. In the 3D case where we let

$$\omega_{\rm HE} \equiv \lim_{\tau \to \infty} \omega_{\rm HE}(\tau) = \lim_{\sigma \to 0} \widehat{\omega}_{\rm HE}(\sigma) \tag{117}$$

we obtain the correct result:  $\omega_{\rm HE}^{(3)} = \Delta P^{(3)} (d_t) \Phi_0^{(3)}$ .

In the present of radicals being scavenged or leaving the surface (or else  $T_1$  processes treated simply, cf. Sec. VII) we will obtain in 2D [by analogy to the derivation of Eq. (112)]

$$\omega_{\rm HE}^{(2)} = \Delta \hat{P}(d_t, k_1) \,\hat{\Phi}_0(k_1) \, n_{\rm B} \tag{118}$$

or a well-defined limiting value.

#### IX. SUMMARY AND FURTHER COMMENTS

We have seen in this work how the change in dimensionality has a profound effect on predicted CIDN(E)P observables due to the important role of the re-encounter mechanism in these phenomena. In two dimensions the re-encounter probability asymptotically approaches unity for long times approximately as  $-\frac{1}{2}\ln\sigma$ with  $\sigma \sim \tau^{-1}$ . This same asymptotic logarithmic character shows up in the time (or  $\sigma$ ) dependent probability of reaction, which approaches unity for long times. It may be ascribed to an effective encounter time which approaches infinity as  $(-\frac{1}{2}\ln\sigma)^{-1}$ . The model for CIDNP in 2D is characterized by the dominant role of the initial encounter for short times just as in 3D, and for a reencounter mechanism for long times again dominated by the effective encounter time which logarithmically approaches infinity. Similar comments apply for CIDEP, except here the effective encounter time one may associate with the exchange depolarization process is the one which logarithmically approaches infinity, so the multiple re-encounter process effectively destroys any CIDEP polarization. Similarly, the Heisenberg exchange probability logarithmically approaches unity with long times.

In "real" situations the polarizing and depolarizing mechanisms are terminated after finite times by a variety of processes such as radical scavenging or radicals leaving the surface or by  $T_1$  processes. Illustrative examples of such effects enabled us to show that the predicted CIDN(E)P observables are characterized by welldefined values, which are typically not their asymptotic values. We do wish to note that the explicit dependence of the polarizations upon the termination processes in two dimensions was treated rather simply in this work; there ultimately are important many-body aspects. Thus, for example, for finite radical concentrations (but not very strong reactivity) a single radical will encounter many other radicals each of which can interfere with the polarizing (and/or reaction) processes of a single radical pair. Related concentration-dependent effects have been studied for three dimensions, <sup>29c, 34</sup> but such effects should be even more important in two di $mensions^{25}$  where the re-encounter process between an individual radical pair will, in principle, continue even while the individual radicals of that pair are undergoing re-encounters with entirely different radicals, because of the unit re-encounter probability. Such processes will still tend to randomize or terminate an individual radical-pair re-emounter process, but the values of the polarization, which depend on the termination times albeit logarithmically, should then be quite sensitive to the many-body nature of such phenomena.

A particular aspect of the two-dimensional problem with which we have not concerned ourselves is the existence and nature of the two-dimensional diffusion coefficient itself. This problem has, for example, been discussed by Saffman and Delbruck<sup>16</sup> for several cases. It is analogous to problems dealt with in the present work, i.e., logarithmic divergences for long times. Thus if one has a finite sheet of dimension  $y_N$ , then they find that  $D_a = D_{SE}^{(2)}(\ln 2y_N - 1/2)$  with  $D_{SE}^{(2)} = k_B T / 4\pi \mu h$  (a Stokes-Einstein coefficient) where  $\mu$  is the sheet viscosity and h its width. [Note that this type of logarithmic factor appears in Eq. (27b) relating effects of  $\sigma$  to  $y_N$ .] Another case they consider is that of finite viscosity of the outer liquid. This would be applicable, e.g., for particles diffusing on a membrane surface and in contact with the external liquid. (It would not be applicable to the diffusion of adsorbed particles on a metal surface under high vacuum conditions.) It yields the result  $D_a = D_{SE}^{(2)} [\ln(\mu h/\mu' a) - 0.5772]$ , where here  $a = \frac{1}{2}d$  and  $\mu'(\ll\mu)$  is the viscosity of the outer liquid. In this case, then there is a well-defined time-indpendent diffusion coefficient. However, when this is not applicable, then they get a time-dependent diffusion coefficient which for long time (or small s) may be written as  $\hat{D}(s) \approx D_{SE}^{(2)} [\ln(4\mu/$  $(\rho a^2 s)^{1/2} = 0.5772$  with  $\rho$  the density of the fluid comprise ing the two-dimensional surface. If such a form is required in a particular problem, then one must solve the Laplace transformed form of the SLE [e.g., Eq. (15)] but with D replaced by  $\tilde{D}(s)$ .<sup>36</sup>

Clearly, the predictions for CIDN(E)P in two dimensions here suggest that if appropriate experiments are feasible, then they would be expected to yield much use-ful information about the relatively unexplored nature of bimolecular encounter processes in two dimensions.

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#### APPENDIX: GLOSSARY OF SYMBOLS

A complete glossary of symbols used in previous three-dimensional theoretical CIDN(E)P studies can be found in Ref. 2(a). We list here the new symbols introduced in this work and those employed previously but of special importance.

$D = D_a + D_b$ Diffusion constant for relative motion of the radical pair	r
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 $D_{\rm SE}^{(2)}$  A "Stokes-Einstein" two-dimensional diffusion coefficient

- $\hat{D}(s)$  s-dependent diffusion coefficient
- $\mathfrak{F}(t), \, \hat{\mathfrak{F}}(s)$  Time dependent probability of radical pair reaction and its modified Laplace-transform where  $\hat{\mathfrak{F}}(s) = s\mathfrak{F}(s)$
- F(r), f(y) Force of interaction between radical pair, with the dimensionless form  $f(y) = dF(r)/k_BT$
- $\hat{\mathfrak{F}}^{*}(t), \hat{\mathfrak{F}}(s)$  Time-dependent probability of reaction of triplets for unit reactivity of singlets and its modified Laplace-transform where  $\hat{\mathfrak{F}}^{*}(s) = s\mathfrak{F}(s)$

$$\mathfrak{F}^*$$
 Long time (i.e.,  $t \to \infty$ ) asymptotic value of  $\mathfrak{F}^*(t)$ 

 $\Phi(t)$  Time-dependent flux of particles into a sphere about a specific target center

 $\Phi_0(t), \Phi_{0,\delta}(t)$  The flux  $\Phi(t)$  for the case  $n_{B,0} = 1$  and its time derivative  $\Phi_{0,\delta}(t) = d\Phi_0(t)/dt$ 

- J(r), j(y) Exchange interaction between radical pair and its dimensionless form
- $j_0$  Dimensionless exchange interaction at y = 1 (or r = d),  $j_0 = J_0 d^2/D$
- $k_B$  Boltzmann constant
- k,  $\kappa$  First order rate constant for radical reaction upon contact and its dimensionless form  $\kappa = kd^2/D$
- $k_0(t)$  Time-dependent source of radicals, usually  $k_0(t) = k_0 U(0)$  [where U(0) is the unit step function]  $\kappa_0 = k_0 d^2/D$
- $k_1, \kappa_1$  First order, spin-dependent radical decay rate constant due to, for example, scavenging processes, and its dimensionless form
- $k_2$  One-half of the rate constant for new bimolecular encounters in 3D

 $x_r, K'$  Space- and spin-dependent reaction operator with its finite difference matrix analogue

- $\mathcal{L}(\sigma) \approx \ln y_N$  A  $\sigma$ -dependent quantity numerically approximating the effects of an outer absorbing boundary,  $\mathcal{L}(\sigma) \approx \ln y_N$
- $\Lambda(t), \hat{\Lambda}(s)$  Time-dependent probability of radical reaction for Q=0 for singlets, with its modified Laplace transform where  $\hat{\Lambda}(s) = s\Lambda(s)$
- $\Lambda \qquad \text{Long-time (i.e., } t \rightarrow \infty) \text{ limiting value of } \Lambda(t)$
- $n_{\rm A}(r,t)$ , Time and space -dependent radical concentrations  $n_{\rm B}(r,t)$
- $n_{A,0}, n_{B,0}$  Initial uniform concentrations of species A and B

 $n_{A}(t), n_{A}(s)$  Time- (or s) dependent concentration of radicals A and B considered uniformly distributed  $n_{B}(t), n_{B}(s)$ 

- $P_a(t)$ ,  $\hat{P}_a(s)$  Time-dependent electron spin polarization of a radical and its s-dependent form. [Note in high magnetic fields  $P_b(t) = -P_a(t)$ ]
- $P_a^{\infty}$  Long time limiting value of  $P_a(t)$

$$\Delta P(y_I \tau)$$
, Time-dependent fractional change in the electron spin polarization from its initial value (and its  $\Delta P(y_I, \sigma)$  modified Laplace transform) given two radical were initially separated by the distance (dimensionless)  $y_I$ 

- $\varphi(t), \hat{\varphi}(s)$  Time-dependent probability that radicals have not reacted to form products,  $\varphi(t)=1-\mathfrak{F}(t)$ , with its modified Laplace transform
- q Dimensionless form of half the difference in ESR resonant frequencies of the two interacting radicals,  $q = Qd^2/D$
- **R** Relaxation matrix containing spatially independent terms
- s Laplace transform variable
- $\sigma$  Dimensionless form of s,  $\sigma = sd^2/D$

t, 
$$\tau$$
 Time variable and its dimensionless form,  $\tau = tD/d^2$ 

 $t_f(y_I, y_N)$  Transfer factor denoting the probability that radicals initially separated at  $y_I$  will eventually come in  $t_f(y_I, \sigma)$  contact before an absorbing wall at distance  $y_N$  interferes with the diffusive process, and its  $\sigma$ -dependent form

 $\tau_1$  Lifetime of the interacting radical pair for contact interactions (i.e., within small spatial region about y = 1),  $\tau_1 = d\Delta r/(2D)$ 

$$\tau_I$$
 Dimensionless analogue of  $\tau_1$ ,  $\tau_I = \Delta y/2 = \tau_1 D/d^2$ 

- $\tau_I^{(2)}, \tau_I^{(3)}$  Effective lifetimes of radical (contact) interactions in two or three dimensions:  $\tau_I^{(2)}(\sigma) \cong \tau_I \mathfrak{L}(\sigma)$ and  $\tau_I^{(3)} = \tau_I$
- $\tau_{J}(t), \tau_{J}$  Time-dependent lifetime of radical pair interaction for spin exchange process and its long time limiting value
- $\tau_1(\lambda)$  Effective lifetime (in seconds) of an exchanging radical pair when the spin exchange process may occur over a finite region of space (i.e.,  $r_{ex}$  finite)

$$\tau_1$$
 Dimensionless form of  $\tau_1(\lambda)$ ,  $\tau_1 = \tau_1(\lambda) D/d^3$ 

- $\tau_{\lambda}^{(2)}, \tau_{\lambda}^{(3)}$  Effective radical exchange lifetimes for  $r_{ox} \sim d$  in two or three dimensions:  $\tau_{\lambda}^{(2)} \cong \tau_{\lambda} \ln y_N \cong \tau_{\lambda} \mathcal{L}(\sigma)$ and  $\tau_{\lambda}^{(3)} \cong \tau_{\lambda}$
- V(i) Finite difference form of the differential y dy written at radical separation  $y_i$
- W Finite difference "transition" matrix which comprises the discrete form of the diffusion operator
- y Dimensionless radical distance y = r/d
- $y_{ex}$  Dimensionless exchange distance,  $y_{ex} = r_{ex}/d$
- y<sub>I</sub> Initial radical separation
- $y_N$  Position of outer absorbing wall

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tions. This could be done by noting first, that our numerical results have shown that  $t \approx s^{-1}$  [cf. Eq. (27)]. Also, Pedersen lin Chap. XVII of Ref. 1(b)] relates the analytic results (for 3D) obtained by using the partially absorbing inner boundary condition of Collins and Kimball [F. Collins and G. Kimball, J. Colloid Sci. 4, 425 (1949)] to those used in the CIDN(E)P formulation, Eq. (13). These results (when extended to 2D) would permit one to use Ref. 8(a) in attempting to calculate  $\hat{\sigma}^{(2)}(\sigma)$  for different initial spatial distributions of the radicals. However, integrals containing Bessel functions would require numerical methods of solution anyway.

- <sup>20</sup>The approximation  $\mathfrak{L}(\sigma) \approx \ln y_N$  used in Eq. (36) can be obtained from Eq. (27b) and the assumption that  $y_N \approx 10$  to 30 represents values of  $\sigma$ , or  $(tD/d^2)^{-1}$  of physical interest. From Eq. (27) one finds this range in  $y_N$  corresponds to diffusive times of about 5 to 1500 nsec previous to scavenging. With  $y_N$  in this range one has to a good approximation  $\frac{2}{3}[\ln y_N - \frac{1}{2}]^{1/2} \approx 1$  [which appears as an intermediate step in the calculation of Eq. (33) from Eq. (27)] yielding our simplified substitution.
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