# Theory of chemically induced dynamic electron polarization. $\Pi^*$

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The earlier theoretical analysis for chemically induced dynamic electron polarization (CIDEP), based on the stochastic-Liouville equation, is generalized to explicitly include the spin-dependent exchange forces in the diffusive trajectories, thus permitting a consistent analysis of the simultaneous effects of exchange on both the spin-selective chemical reaction and CIDEP effects. The semiclassical treatment of diffusion under a "classical" force field due to the valence interactions requires the introduction of spin-dependent diffusive and reactive trajectories, and this is discussed for the Brownian-motion model utilized. Our results show that the polarization generated per fractional probability that singlets react  $(P^{\infty}/3)$ , is not sensitive to the actual details of the spin-selective reactive process (although the absolute polarization  $P^{\infty}$  is sensitive to the reactive process), due presumably to the spatial distinction between interradical separations (r) for which the reaction may occur vs those for which CIDEP polarizations are developed. The former require  $\hbar |J(r)|/kT > 1$  while for the latter  $\hbar |J(r)|/kT < 1$ , where J(r)is the exchange interaction. It is found that differences in the (nonreactive) diffusive trajectories for singlets and triplets give polarizations that are generally negligible compared to those which develop as a result of the spin-selective reaction (for our overdamped diffusive model). However, our results for more long-range Coulomb interactions between charged radicals show they can produce significant changes on  $P^{\infty}/3$  that are quite sensitive to the magnitude of J. Thus ionic-concentration effects on  $P^{\infty/\mathfrak{F}}$  should be an important indicator of the CIDEP mechanism. Results are also given for the spin-depolarization process, whereby the effects of spin exchange on a radical pair, which initially collide with residual nonthermal polarization, are to destroy this polarization. The effective range of the spin exchange is found to be weakly enhanced as the range of J(r) is increased. Also, it is shown that, for several variations of a simple exponential dependence of J(r) on r,  $P^{\infty}/F$  is hardly affected, although nonexponential dependences can introduce marked changes.

#### I. INTRODUCTION

In Paper  $I^1$  of this series we developed a detailed theoretical analysis of the phenomenon of chemically induced dynamic electron polarization (CIDEP) based on our earlier preliminary account.<sup>2</sup> In that work we employed a fairly simple description of the combined effects of the relative diffusion of the radical pair and of the possibility of their engaging in a spin-selective chemical reaction, which could initiate the spin polarization process. That is, the diffusion was treated as that for simple Brownian diffusion; the effects of the valence forces (which can become very large) on this diffusion were ignored for simplicity. Second, the effects of a spinselective chemical reaction were introduced phenomenologically by a simple irreversible (in the chemical-kinetic sense) "first-order chemical rate constant" giving the probability of the radical pair reacting per unit time as a function of the interradical separation.

It is clear that a more rigorous treatment should include the valence forces in an explicit manner and, in particular, one that is consistent with the inclusion of the exchange forces in the spin Hamiltonian. One would then want to include the effect of such forces on the relative diffusive motion of the radicals, while at the same time recognizing that these forces are the fundamental cause of the chemical reactions. In fact, one should expect to treat the processes in a manner analogous to reactive-collision theory, but in liquids, of course, the diffusive damping of molecular trajectories plays a very important role.

We have, in the present work, introduced explicitly in a relatively simple fashion, the effects of valence forces into the diffusive reactive trajectories in order to attempt a more realistic treatment of the CIDEP phenomenon. We continue to apply semiclassical theory such that the spins are treated quantum mechanically, while the molecular motions are treated classically. We also continue to employ Brownian motion theory for describing the molecular motions. But now the valence forces may become the potential terms in the generalized Fokker-Planck equation for the combined configuration and momentum phase space.<sup>3</sup> This wellknown general expression for Browian motion is itself the classic example of a stochastic Liouville equation.<sup>4</sup> Actually, for the sake of simplicity, we consider the limiting form of the Fokker-Planck equation for just configuration space (the Smoluchowski equation). The use of this latter, simplified, expression actually implies the restrictions that (1) dynamics only over times long compared to diffusive damping times,  $\beta^{-1}$ , are properly described and (2) oscillatory type behavior due to motion with substantial valence forces is taken as being overdamped, e.g., if **F** represents such forces, then one is assuming  $|\text{div } \mathbf{F}| \ll \mu\beta$ , where  $\mu$  is an appropriate reduced mass.<sup>3</sup> (A convenient way of physically regarding the Smoluchowski equation is as the limit when  $\beta \rightarrow \infty$  but  $D = kT/\mu\beta$  remains finite.) It is perhaps this overdamped feature of the Smoluchowski equation which is most unrealistic in terms of representing diffusion in a classical force field due to the valence interactions.

Given these assumptions, it would be a simple matter to write down the Smoluchowski equation for an arbitrary valence force field. However, one must note that for a spin-selective chemical reaction of radical pairs (e.g., one where singlets react but triplets are repelled) the adiabatic potential surfaces for the reaction are themselves spin dependent. Thus, when one writes the stochastic-Liouville equation for the spin-density matrix, the diffusion operator must now become spin dependent, e.g., the density-matrix elements that are pure singlet (triplet) must follow singlet (triplet) trajectories, while the off-diagonal density-matrix elements of mixed character must follow some intermediate trajectory.

These arguments, which naturally point out the need for a spin-dependent diffusion operator in the stochastic-Liouville equation for the spin-density matrix, have another important implication. There is a well-known fundamental problem with all semiclassical theories of spin relaxation be they of more conventional varieties or based on the stochastic-Liouville equation, viz., the spins tend to relax to thermal equilibrium at infinite temperature and one must make ad hoc corrections to cause the spins to relax to the temperature of the bath. However, the use of a spin-dependent potential in the stochastic-Liouville equation, as we have outlined above, will tend to cause spins of each multiplicity to relax to their correct spatial equilibrium distributions, by virtue of the fact that a particular Fokker-Planck (or Smoluchowski) equation yields the correct Boltzmann distribution in the long-time limit.<sup>3</sup> That is, by the use of spin-dependent diffusion in the otherwise classical description of the motion of the molecules, one is also including some of the effects of the "back reaction" of spins on the "lattice." Normally, spin-dependent forces are quite negligible in their effects on the motions of the lattice, but when one is dealing with large valence interactions which are spin dependent, viz., exchange interactions, this is no longer so and such matters as achieving correct Boltzmann distributions are at least as important as are the effects of such interactions on the diffusive trajectories.

In the light of the above introduction, some of the questions which we seek to answer are: (1) Will the differences in diffusive trajectories for singlet and triplet spins yield net differences in their spin populations in regions of space where spin polarization is an effective mechanism; and more important (2) to what extent are the predictions on CIDEP polarizations sensitive to the details of the valence forces and reactive trajectories? We also consider in this work the importance of (3) the exact form of the radial dependence of the exchange interaction, (4) Coulombic interactions between charged radical pairs, and (5) the details of the spin-depolarization process, whereby a radical pair, which initially collides with residual nonthermal polarization, has this polarization destroyed by Heisenberg spin exchange (HE) (cf. I). All these matters are conveniently dealt with by the present formalism.

#### II. METHODS

We shall, as in I, use the stochastic-Liouville equation

$$\partial \rho(\mathbf{r}_i, t) / \partial t = -i \mathcal{K}^{\times}(\mathbf{r}_i) \rho(\mathbf{r}_i, t) + D\Gamma_{\mathbf{r}} \rho(\mathbf{r}_i, t)$$
(1)

to describe the spin dynamics of a pair of radicals a and b under the combined effect of spin interaction and relative diffusion. We again write the Hamiltonian  $\mathcal{K}(\mathbf{r}_i)$  in the high-field approximation as

$$\mathcal{K}(\mathbf{r}_{i}) = \mathcal{K}^{0}(\mathbf{r}_{a}, \mathbf{r}_{b}) + \mathcal{K}' \quad , \tag{2}$$

where  $\mathfrak{H}^{0}(\mathbf{r}_{a}, \mathbf{r}_{b})$  is that part of  $\mathfrak{K}(\mathbf{r}_{i})$  which is diagonal in the singlet-triplet representation and includes the exchange interaction  $-J(\mathbf{r}_{a}, \mathbf{r}_{b})$  ( $\frac{1}{2} + 2\mathbf{S}_{a} \cdot \mathbf{S}_{b}$ ), while the off-diagonal part  $\mathfrak{K}'$  is independent of  $\mathbf{r}_{i}$ and consists only of differences in g values and hyperfine energies between the two interacting radicals. One may then write<sup>1</sup>

$$\mathcal{H}' = Q(S_{ag} - S_{bg}) \quad , \tag{3a}$$

where

$$Q = \frac{1}{2} \left( g_{\mathbf{a}} - g_{\mathbf{b}} \right) \beta_e \hbar^{-1} B_0 + \left( \sum_j A_j^{\mathbf{a}} A_j^{\mathbf{a}} - \sum_k A_k^{\mathbf{b}} M_k^{\mathbf{b}} \right)$$
(3b)

and for simplicity we again let  $J(\mathbf{r}_{a}, \mathbf{r}_{b}) = J(r)$ , where r is the distance between the two radicals, so that  $\mathcal{H}_{0} = \mathcal{H}_{0}(r)$ .

However, as distinct from I, we want the diffusion operator  $D\Gamma_r$  to include effects of attraction (or repulsion) between the radicals a and b. This is formally equivalent to the well-known problem of the movement of a Brownian particle in a potential field and the (Smoluchowski) diffusion operator for the classical probability distribution p is given by

$$D\Gamma_{\mathbf{r}}p(\mathbf{r}) = D\nabla \cdot \left[\nabla p + (1/kT)p\nabla U(r)\right] , \qquad (4)$$

where  $D = D_a + D_b$  is the diffusion coefficient for the

relative motion between radicals a and b and U(r) is the potential energy between them assumed to depend only on r. Furthermore, we shall allow U(r) to be spin dependent; hence  $D\Gamma_{\mathbf{r}}$  now becomes a spin- as well as  $\mathbf{r}$ - dependent operator.

We now define a function F(r) as

$$F(r) = (1/kT)\nabla U(r) = (1/kT)[\partial U(r)/\partial r]$$
(5)

[where F(r) is however an operator in spin space] and then take advantage of the orientation independence of  $\mathcal{H}_0(r)$  and F(r) to obtain the following equation for  $\hat{\rho}(r, t) = r\rho(r, t)$  [i.e.,  $r\rho(\mathbf{r}_i, t)$  averaged over orientations]:

$$\partial \hat{\rho}(r,t) / \partial t = -i \mathcal{K}^{*}(r) \hat{\rho}(r,t) + D \hat{\Gamma}_{r} \hat{\rho}(r,t) , \qquad (6)$$

where

$$\hat{\Gamma}_{r}\hat{\rho}(r,t) = \left[\partial^{2}\hat{\rho}(r,t)/\partial r^{2}\right] + (1/r)\left\{\partial/\partial r\right\}\left[\hat{F}(r)\hat{\rho}(r,t)\right]$$
  
and  $\hat{F}(r) = rF(r)$ . (7)

The polarization at time t of radical a is given by

$$P_{\mathbf{a}}(t) = -2 \operatorname{Tr}[\rho(t)S_{\mathbf{a}\mathbf{s}}] \quad , \tag{8}$$

where

$$\rho(t) = \int_0^\infty r \hat{\rho}(r, t) dr \quad . \tag{9}$$

We are usually interested in the polarization at the end of a collision, i.e.,  $P_a^{\infty} \equiv \lim_{t \to \infty} P_a(t)$ . Then one has<sup>1</sup>

$$P_{a}^{\infty} = -2 \limsup_{s \to 0} \int_{0}^{\infty} r \operatorname{Tr}[S_{as}\widetilde{\rho}(r,s)] dr$$
$$\simeq -2 \operatorname{Re} \lim_{s \to 0} \int_{0}^{\infty} r \rho_{ST_{0}}(r,s) dr \quad , \tag{10}$$

where  $\tilde{\rho}(r, s)$  is the Laplace transform of  $\hat{\rho}(r, t)$  and the approximate equality represents the use of the high-field approximation, so only the S and  $T_0$ states are important.<sup>1</sup>

We again solve

$$[s+i\mathcal{H}^{\mathsf{x}} - D\hat{\Gamma}_{r}]\rho(r,s) = \hat{\rho}(r,t=0) \equiv \hat{\rho}_{0}(r)$$
(11)

by the finite-difference technique already extensively described in I, i.e., we rewrite Eq. 11 as

$$[s\mathbf{1} + i\,\mathbf{\Omega} - D\mathbf{W}]\hat{\boldsymbol{\rho}}(s) = \hat{\boldsymbol{\rho}}(0) \quad , \tag{12}$$

where  $\hat{\rho}(s)$  and  $\hat{\rho}(0)$  are vectors in a 4(N+1)-dimensional space formed from the direct product of a 4-dimensional spin space with N+1 discrete values of r. Also 1 is the unit matrix,  $\Omega$  is the matrix of elements of the operator  $\mathcal{R}^{x}$ , and W is the transition matrix obtained by applying the finite-difference technique to the diffusion operator  $\hat{\Gamma}_{r}$ . The  $\Omega$  matrix is identical to that used in I, but the W matrix is different due to (1) the inclusion of potential forces and (2) the spin dependence of  $\hat{\Gamma}_{r}$ . We illustrate the effects of the spin dependence of  $\hat{\Gamma}_{r}$  by writing  $i\mathcal{H}^{x} - D\hat{\Gamma}_{r}$  of Eq. (11) in the 4-dimensional spin space for states S and  $T_{0}$  in which  $\hat{\Gamma}_{r}$  is naturally defined. That is

$$i_{3}C^{*} - D\hat{\Gamma}_{r} = \begin{pmatrix} D\hat{\Gamma}_{r,SS} & -iQ & iQ & 0\\ -iQ & i2J(r) - D\hat{\Gamma}_{r,ST} & 0 & iQ\\ iQ & 0 & -2iJ(r) - D\hat{\Gamma}_{r,TS} & -iQ\\ 0 & iQ & iQ & -D\hat{\Gamma}_{r,TT} \end{pmatrix}.$$
(13)

Here  $\hat{\Gamma}_{r,SS}$  and  $\hat{\Gamma}_{r,TT}$  are, respectively, the diffusion operators for singlet and triplet states.<sup>5</sup> By a simple generalization of our discussion of the inclusion of spin-selective chemical reactions,<sup>1</sup> we note that for the off-diagonal elements, e.g.,  $\rho_{ST_0}$  the proper diffusion operators should be

$$\hat{\Gamma}_{r,ST} = \hat{\Gamma}_{r,TS} = \frac{1}{2} (\hat{\Gamma}_{r,SS} + \hat{\Gamma}_{r,TT}).$$
(14)

That is, physically, regarding  $\hat{\Gamma}_r$  from a finitedifference point of view, it gives the jump rate between different values of r. As such,  $\hat{\Gamma}_{r,SS}$  and  $\hat{\Gamma}_{r,TT}$  yield the lifetime-uncertainty broadening of the S and  $T_0$  states at a specific position r due to jumps to other positions. Then Eq. (14) follows from the usual uncertainty-in-lifetime effects for off-diagonal density-matrix elements.<sup>6-9</sup>

We now give the resulting  $\mathbf{W}^{\alpha}$  matrix appropriate for each N+1-dimensional subspace corresponding to  $\alpha = SS$ ,  $ST_0$ ,  $T_0S$ , or  $T_0T_0$ :

$$D^{-1}W^{\alpha}_{0,0} = -(2/\Delta r^2)(1 + \Delta r/d) + r_1 F_{\alpha}(1)/\Delta rr_0 , \quad (15a)$$

$$D^{-1}W_{0,1}^{\alpha} = 2/\Delta \gamma^{2} + F_{\alpha}(0)/\Delta \gamma \quad , \tag{15b}$$

$$D^{-1}W_{j,j-1}^{\alpha} = \Delta r^{-2} - F_{\alpha}(j)/2\Delta r \quad , \tag{16a}$$

$$D^{-1}W_{j,j}^{\alpha} = -\frac{2}{\Delta \gamma^2} + (2\Delta \gamma)^{-1} [F_{\alpha}(j+1)r_{j+1}/r_j]$$

$$-F_{\alpha}(j-1)r_{j-1}/r_{j}$$
, (16b)

$$D^{-1}W^{\alpha}_{j,j+1} = \Delta \gamma^{-2} + F_{\alpha}(j)/2\Delta \gamma \quad , \qquad (16c)$$

where 0 < j < M, and

$$D^{-1}W^{\alpha}_{M,M-1} = 2/(1+f)\Delta \gamma^2 - F_{\alpha}(M)/\Delta \gamma(1+f) , \quad (17a)$$

$$D^{-\lambda}W^{\alpha}_{M,M} = -\frac{2}{f}\Delta\gamma^{2} - F_{\alpha}(M-1)r_{M-1}/r_{M}\Delta \ (1+f) \quad ,$$
(17b)

$$D^{-1}W^{\alpha}_{M,M+1} = 2/f(1+f)\Delta\gamma^2 \quad ; \qquad (17c)$$

while for M < j < N,

$$D^{-1}W_{j,j-1}^{\alpha} = 1/f^2 \Delta r^2 \quad , \tag{18a}$$

$$D^{-1}W_{j,j}^{\alpha} = -\frac{2}{f^2} \Delta r^2 \quad , \tag{18b}$$

$$D^{-1}W^{\alpha}_{j,j+1} = 1/f^2 \Delta r^2 \quad ; \tag{18c}$$

in addition

$$D^{-1}W_{N-1,N}^{\alpha} = 0 \quad . \tag{19a}$$

$$D^{-1}W^{\alpha}_{N,N-1} = 2/f^2 \Delta r^2 \quad , \tag{19b}$$

$$D^{-1}W_{N,N}^{\alpha} = 0 \quad . \tag{19c}$$

Note that in Eqs. (15) and (16)  $\Delta r$  is the distance between the  $j^{th}$  and  $(j-1)^{th}$  adjacent positions, where  $j \leq M$ , i.e.,  $r_j = r_{j-1} + \Delta r$ . Also  $r_0 = d$ , the distance of closest approach. For j > M,  $r_j - r_{j-1}$  $= f \Delta r$  and M is chosen so that  $J(r_M) \approx 0$  and  $F_{\alpha}(r_M)$  $= F_a(M) \approx 0$ . That is, for  $r < r_M$ , there is an r-dependent exchange interaction and a potential field against which the diffusion takes place and small increments of  $\Delta r$  are required for a proper solution; while for  $r > r_M$ , the Hamiltonian  $\mathcal{H}(r)$  is independent of r and the diffusion is simple unhindered Brownian, so larger increments  $f \Delta r$  with  $f \sim 10-20$ may be utilized to adequately represent the motion. We have already pointed out in Paper I that the use of a finite-difference technique corresponds to a description of the diffusion by a discrete master equation. Thus, when there are restoring forces, one usually inposes the further condition on the size of  $\Delta r$  (beyond those given in I) that it be small enough that the off-diagonal elements of W are nonnegative, while the diagonal elements of W must be nonpositive.<sup>10,11</sup> It then follows from Eqs. (15)-(19) that

$$\Delta r < \left| 2/F_a(j) \right| \quad , \tag{20}$$

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

As we have done in Paper I, we have incorporated an absorbing wall at  $r = r_N$ , so that, whenever the two radicals have separated by  $r_N$ , they may not diffuse together again. By choosing  $r_N$  sufficiently large, convergent results may be obtained.<sup>1</sup> In I a reflecting wall at r = d was included. In principle, our explicit inclusion of valence forces removes the need for such a boundary condition, but we have found it useful nevertheless.

The condition of conservation of total probability

$$\sum_{i=0}^{N} V(i) W_{i,j}^{\alpha} = 0 \quad \text{for } j = 0, 1, \dots, N$$
 (21)

has been used extensively (cf. I) to obtain Eqs. (15)-(19). The radial weighting factors V(i) are given in I [Eq. (2, 27)].

Note that in finite-difference notation Eq. (10) becomes

$$P_{a}^{\infty} = -2 \operatorname{Re} \lim_{s \to 0} \sum_{i=1}^{N} V(i) \tilde{\rho}_{ST_{0}}(i, s) ; \qquad (22a)$$

but in the present case, where valence forces can explicitly lead to "bonding" in which  $r \approx d$  for long periods, it is often more useful to consider

$$P_{a}^{\infty}(N) = -2 \operatorname{Re} \lim_{s \to 0} \tilde{\rho}_{ST_{0}}(N, s) \quad , \qquad (22b)$$

which represents just the separated particles at  $t \rightarrow \infty$ . Similarly, the probability of survival per collision  $\sigma$  is given as<sup>1</sup>

$$p = \lim_{s \to 0} \sum_{i=1}^{N} V(i) [\tilde{\rho}(i, s)_{SS} + \tilde{\rho}(i, s)_{T_0 T_0}] \quad , \qquad (23a)$$

where (since  $T_{\pm}$  states are being neglected, cf. I):

$$\sum_{i=1}^{N} V(i) [\hat{\rho}(i, 0)_{SS} + \hat{\rho}(i, 0)_{T_0^{T_0}}] = 1$$

i.e., the density matrix is normalized at time zero. However, the fraction of particles which have separated at  $t \rightarrow \infty$  is

$$P(N) = \limsup_{s \to 0} V(N) [\tilde{\rho}(N, s)_{SS} + \tilde{\rho}(i, s)_{T_0 T_0}] \quad . \quad (23b)$$

For the probability of reaction during a collision one has

$$\mathfrak{F} = 1 - \mathfrak{O} \text{ or } \mathfrak{F}(N) = 1 - \mathfrak{O}(N)$$
 (24)

In Paper I, where the spin-selective chemical reaction was represented by an irreversible chemical rate, which merely "destroys" radical, one had  $P_{\mathbf{a}}^{\infty} = P_{\mathbf{a}}^{\infty}(N), \ \Theta = \Theta(N), \ \text{and} \ \mathfrak{F} = \mathfrak{F}(N).$  In the present case, the trapped singlet radical pairs at  $r \approx d$  are not lost to the system, so that  $\mathcal{P}(t) = 1$  for all t [note  $\mathcal{O} \equiv \lim_{t \to \infty} \mathcal{O}(t)$ , etc.] and properly one should look at the  $P_a^{\infty}(N)$ ,  $\mathcal{O}(N)$ , etc., for the separated radicals, which contribute to the ESR spectrum. However, we note that the diffusion Eq. (4) automatically includes detailed balance, so that as long as U(r) remains finite, there will still be a finite probability that a "bound" pair of radicals can separate even though U(r=d) is very large. But, because the absorbing wall at  $r = r_N$  is kinetically irreversible (representing, in a sense, infinite space for the relative diffusion of a single radical pair) as  $t = \infty$  even the "tightly bound" pairs must separate to  $r_N$ . This feature can be overcome by either (1) considering finite but long times and by studying  $P_{a}(N, t)$ , etc., or by (2) introducing (similar to I) an irreversible kinetic process which



FIG. 1. Spin Dependent Potentials  $U_{\alpha}(r)$  as a function of r the internadical separation. The solid curves labeled S and T represent the exchange potentials utilized for singlet and triplet states respectively, with a reflecting wall at r=d. The dashed lines represent the usual continuation of the potentials in the absence of a reflecting wall (cf. text).

permanently removes the strongly bound radical pairs as they form by valence attractions and by studying  $P_a^{\infty} = P_a^{\infty}(N)$ , P = P(N). We have used Method (2) primarily because of its computational convenience, but we have made some efforts at a comparison of results for the two methods. We consider this irreversible kinetic process after our discussion of potential surfaces.

#### A. Potential Surfaces

We show in Fig. 1 the representation of  $U_{\alpha}(r)$ which we have employed. This has been chosen by analogy to the well-studied, hydrogen-atom-pair potential surfaces<sup>12</sup> as well as for computational convenience. That is we write  $U_{ss}(r) \cong (H_0 + H_1)/$ (1+S) and  $U_{TT}(r) \cong (H_0 - H_1)/(1+S)$ , where  $H_0$  is the "Coulomb integral,"  $H_1$  is the exchange integral which we shall write as  $-\hbar J(r)$ , and S the overlap integral. The usual S and T energy surfaces are shown by the solid curves for r > d and the dashed curves for r < d. We take d to be the interradical distance characteristic of the stable bond. As noted above, we introduce a reflecting wall at r = d[i.e.,  $U_{ss}(r) = U_{TT}(d) = \infty$  for r < d] as a convenient approximation to the repulsive terms which dominate both the S and T curves at short internuclear distances. Then for r > d we note that usually  $H_1$ is several times larger than  $H_0$  and is the main source of the attractive forces, while S tends to be small.<sup>12</sup> Thus for convenience we let

$$U_{SS}(r) \approx -U_{TT}(r) \approx -\hbar J(r) \quad r > d \tag{25}$$

and it is reasonable to approximate J(r) for r > dby an exponential decay in r:

$$J(r) = J_0 \exp[-\lambda(r-d)] \quad r \ge d \quad . \tag{26}$$

[While Eqs. (25) and (26) (and Fig. 1) represent the forms of the potentials we have employed in most of our computations, we have also considered effects of Coulomb-type attractions and repulsions which contribute equally to both S and T potential surfaces as well as some variation of J(r) from that given in Eq. (26) (see Sec. III).] It follows from Eq. (5), that

$$F_{SS}(r) = -F_{TT}(r) = (\lambda \hbar J_0 / kT) \exp[-\lambda (r-d)] \quad (27a)$$

and from Eq. (14) that

$$F_{ST_0}(r) = F_{T_0S}(r) = \frac{1}{2} [F_{SS}(r) + F_{TT}(r)] = 0$$
 . (27b)

That is, while the singlet terms in  $\rho$  diffuse under an attractive potential and the triplet terms under a repulsive potential, the  $\rho_{s,r_0}$  terms experience normal Brownian diffusion.<sup>13</sup>

We now define a "first-order chemical rate constant" k(r) which gives the rate at which a singlet radical pair, tightly bound by the attractive valence forces between singlets [i.e.,  $F_{ss}(r \approx d)$ ], is irreversibly removed from the system, so that it can never again dissociate even as  $t \rightarrow \infty$  [cf. discussion after Eq. (24)]. We use the simple form

$$k(\boldsymbol{\gamma}_i) = k \delta_{i,0} \quad , \tag{28}$$

so that only the singlet radical pairs in the contact range d to  $d + \Delta r$  are affected. This is indicated in Fig. 1. In this application, the use of k is thus largely that of a computational artifact. A large value of k guarantees that the singlet radical pair remains bound, while a small value of k does not fully prevent them from separating as  $t \rightarrow \infty$ . For comparison purposes, calculations also are performed for  $F_{SS}(r) = F_{TT}(r) = 0$ , i.e., for exchange forces absent (EFA), but  $k \neq 0$ . This case is very similar to (but not the same as) the model used in I. For the EFA case, one can only rely on the effects of the irreversible process with rate constant k, to deplete singlet radical pairs. The difference between the EFA case used here and that in I is that, in the latter, off-diagonal elements  $\rho_{S,T_0}(d)$  were taken to decay with rate constant  $\frac{1}{2}k$ , while in the present work they do not. The present choice is made, because from Eq. (27b), the  $\rho_{S,T_0}(d)$ elements are not "trapped" by the valence forces, so that it is inappropriate to irreversibly remove them from the system when dealing with the model in which the exchange forces are present (EFP), and as noted EFA is meant for comparison with EFP. These distinctions do have physical consequences which will be enumerated in Sec. III.

## **B.** Initial Conditions

In Paper I the initial condition of  $\rho_0(r) = \rho_0 \delta(r)$  $-r_0/r_0^2$  (where  $\rho_0$  is the initial r-independent spindensity matrix) was utilized throughout, since for the models considered there, either (1) polarizations started upon initial formation of the radical pair or (2) equal amounts of S and  $T_0$  radical pairs formed from random encounters had to reach  $r_0 = d$ to react by the spin-selective chemical reaction before the polarization could begin. For the current models being considered, the very diffusion rates, as well as relative equilibrium probability distributions, differ for the S and  $T_0$  spins, and this can only be properly considered by starting the radical pair initially at  $\rho_0(r) = \rho_0 \delta(r - r_I) / r_I^2$ , where  $J(r_I)$  $\approx 0$ , etc., i.e., the interradical separation is large enough that their various interactions are negligible. We, therefore, can again use the standard Brownian motion result for the "rate constant" of new bimolecular collisions which produce either S or  $T_0$  states<sup>1,3</sup>:

$$k_2(r_I) = 2\pi r_I D \quad . \tag{29}$$

The appropriate CIDEP intensity  $I_a$ , contribution is [cf. I, Eq. (4.6)]

$$(dI_{a}/dt)_{k_{2}} = k_{2}(r_{I})m_{a}(t)m_{b}(t)[P_{a}^{\infty}(r_{I}) - \Delta P(r_{I})2\operatorname{Re}_{\rho_{S,T_{0}}}(t)],$$

where the explicit dependence on initial  $r_I$  is indicated and  $n_a(t)$  and  $n_b(t)$  are the number densities of radicals a and b.  $\Delta P(r_I)$  is defined as the fractional change in polarization which exists at the onset of the collision and is discussed below. Now, if the effect of valence forces on the diffusive motion were neglected as in I, then the first term in Eq. (30) could equally well be written as

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

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

$$k_2(d)P_a^{\infty}(d) = k_2(\gamma_I)P_a^{\infty}(\gamma_I) \quad . \tag{31}$$

To get around the arbitrariness of initial condition  $r_{I}$ , we usually employ a *transferred* polarization  $P_{a}^{c}(d_{t})$  as

$$P_{a}^{\infty}(d_{t}) = [k_{2}(r_{I})/k_{2}(d)]P_{a}^{\infty}(r_{I}) = (r_{I}/d)P_{a}^{\infty}(r_{I})$$

$$\xrightarrow{\text{finite}} d^{-1}(r_{I}^{-1} - r_{N}^{-1})^{-1}(1 - d/r_{N})P_{a}^{\infty}(r_{I}) , \quad (32)$$

where the arrow points to the expression corrected for an absorbing wall at  $r = r_N$  (cf. Ref. 21 in I). Note that when the effects of valence forces on the diffusion are included, then  $P_a^{\infty}(d_t)$  is no longer the true polarization developed with initial condition r = d, but this definition allows us to compare results of  $P_a^{\infty}(d_t)$  for different initial values of rwithout having to correct for the differences in  $k_d(r_I)$ .

## C. Dimensionless Units

It follows from our above discussion and that of Paper I (cf. Sec. III) that our expressions may be written in dimensionless units, that is,

$$P_{a}^{\infty}(d_{t}) = P_{a}^{\infty}(J_{0}d^{2}/D, Qd^{2}/D, r_{EX}/d, \hbar J_{0}/kT) \quad (33)$$

with equivalent functional dependences for the transferred  $\mathfrak{F}(d_t)$  and  $\Delta P(d_t)$ . [Note that the irreversible rate constant of Eq. (28) introduces the further dimensionless variables,  $kd^2/D$  and  $\Delta r/d$ .] Here  $r_{\rm EX} = \lambda^{-1}5 \ln 10$  [i.e.,  $J(r + r_{\rm EX}) = 10^{-5}J(r)$ ]. As we have found in I, the dimensionless variables are useful for establishing convenient relationships, while the normal physical variables are more directly useful for comparison with experiments.

## **D.** Polarization Quenching

As we have already noted, the quenching of initial polarization due to Heisenberg spin exchange (HE) upon a random collision is also an important process, if the over-all kinetics of the problem is to be dealt with adequately, such as by Eq. (30). This polarization quenching can take place even when the bimolecular collision does not induce any spin-selective chemical reaction.

The polarization quenching is readily obtained by our methods described in I and above. One has only to select as the initial condition that  $2 \operatorname{Re}_{\rho_{s,r_0}} = 1$  [cf. Eq. (30)] or more precisely

$$2\operatorname{Re}_{\rho_{S,T_o}}(r) = \delta(r - r_I)/r_I^2$$
(34)

(while the other initial values are  $\rho_{SS} = \rho_{TT} = \text{Im}\rho_{S,T_0} = 0$ ). The calculation based on Eqs. (6) and (10) then leads to

$$-\Delta P(\gamma_{I}) = P_{a}^{\infty}[\gamma_{I}, \rho_{S, T_{0}}(t) \neq 0] - 1 \quad , \tag{35}$$

where  $P_a^{\infty}[r_I, \rho_{S,T_0}(t) \neq 0]$  is the polarization which remains at the end of the collision, after having started with the initial condition given by Eq. (34). The quantity  $\Delta P(r_I)$  appears in Eq. (30) and the validity of Eq. (35) rests on recognizing that Eq. (1) is linear and homogeneous in  $\rho(r, t)$  so one may superpose solutions obtained for simple initial conditions to obtain solutions for the more complex initial conditions. We can again define a transferred  $\Delta P(d_t)$  in exactly the same manner as Eq. (32) for  $P_a^{\infty}(d_t)$ . Note, however, that  $\Delta P(d_t)$  is not equal to  $\Delta P(d)$  for finite values of  $J_0$  and  $r_{\rm EX}$ , since the spin depolarization by HE will start for  $r_I > d$  as long as  $|J(r_I)| > 0$ . Note also, that by Eq. (27b)

28	7	5

$J_0(\sec^{-1})$	$k(\sec^{-1})$	$P^{\infty}  imes 10^3$	Ŧ	$P^{\infty}  imes 10^3 / \mathfrak{F}$
1011	1014	21.4 (21.4)	0.520 (0.519)	41.2 (41.2)
$(0.0025 \ kT)$	$10^{12}$	10.5 (10.45)	0.254 (0.254)	41.2 (41.2)
	10 <sup>10</sup>	0.198 (0.200)	$4.88 \times 10^{-3}$ (4.86 × 10^{-3})	40.7 (41.2)
	$10^{8}$	$-4.7 \times 10^{-4}$ (2.02×10 <sup>-3</sup> )	$5.92 \times 10^{-5}$ (4.91 × 10 <sup>-5</sup> )	-9.5 (41.2)
	0	$-8.5 \times 10^{-3}$ (0)	0	
10 <sup>13</sup>	1014	7.99 (7.82)	0.529 (0.518)	15,1 (15,1)
$(0.25 \ kT)$	$10^{12}$	4.36 (3.76)	0.289 (0.253)	15.1 (15.1)
	10 <sup>10</sup>	$9.06 \times 10^{-2}$ (7.21×10 <sup>-2</sup> )	$6.2 \times 10^{-3}$ (4.86 $\times 10^{-3}$ )	14.5 (15.1)
	$10^{8}$	$-2.5 \times 10^{-3}$ (7.28×10 <sup>-4</sup> )	$6.3 \times 10^{-5}$ (4.91×10 <sup>-5</sup> )	-39.9 (15.1)
	0	$-3.5 \times 10^{-3}$ (0)	0	
10 <sup>14</sup>	10 <sup>14</sup>	. 8.77 (7.68)	0.592 (0.519)	14.83 (14.84)
(2.5 kT)	$10^{12}$	7.99 (3.76)	0.539 (0.253)	14.83 (14.84)
	$10^{10}$	0.800 (7.21×10 <sup>-2</sup> )	$5.4 \times 10^{-2}$ (4.86 × 10^{-3})	14.77 (14.84)
	$10^{8}$	4.85×10 <sup>-3</sup> (7.28×10 <sup>-4</sup> )	6.0×10 <sup>-4</sup> (4.91×10 <sup>-5</sup> )	8.14 (14.84)
$4 \times 10^{14}$	10 <sup>14</sup>	9.68 (7.59)	0.659 (0.517)	14.68 (14.69)
$(10 \ kT)$	10 <sup>12</sup>	9.68 (3.72)	0.659 (0.253)	14.68 (14.69)
	10 <sup>10</sup>	9.64 (7.14 $\times$ 10 <sup>-2</sup> )	$0.656 (4.86 \times 10^{-3})$	14.68 (14.69)
	10 <sup>8</sup>	6.86 (7.20×10 <sup>-4</sup> )	$0.467 (4.91 \times 10^{-5})$	14.68 (14.69)
$1 \times 10^{15}$	<b>10<sup>14</sup></b>	10.3 (7.54)	0.705 (0.517)	14.6 (14.6)
(25 kT)	$10^{12}$	10.3 (3.69)	0.705 (0.253)	14.6 (14.6)
	10 <sup>10</sup>	10.3 (7.09 $\times$ 10 <sup>-2</sup> )	0.705 (4.86×10 <sup>-3</sup> )	14.6 (14.6)
	108	10.3 (7.16×10 <sup>-4</sup> )	0.705 (4.91×10 <sup>-5</sup> )	14.6 (14.6)

TABLE I. Effects of diffusion under exchange forces on polarization and spin-selective reaction.<sup>a,b</sup>

<sup>a</sup>Values are given both with the exchange forces of Eqs. (4), (5), and (27), and in the absence of these exchage forces for comparison. The latter are in parentheses. The random initial condition is assumed. All values are transferred results for  $r_t = d$ , cf. Eq. (32). k is defined by Eq. (28).

<sup>b</sup>Values of the other parameters used are:  $Q=1\times10^8$  sec<sup>-1</sup>,  $D=10^{-5}$  cm<sup>2</sup>/sec, d=4 Å,  $r_{EX}$ =4 Å,  $\Delta r = 0.05$  Å, M=160, N=360, f=20,  $r_N=212$  Å,  $r_I=11.85$  Å,  $kT/\hbar=4\times10^{13}$  sec<sup>-1</sup>,  $s\Delta r^2/D=10^{-18}$ . Results scale according to Eq. (33), etc.

the diffusion of  $\rho_{ST_0}$  is unaffected by the valence forces illustrated in Fig. 1, and also that the depolarization, even for random collisions, begins well before radicals approach near to d (i.e., the region where valence forces may significantly affect the motions).

It follows from Eq. (30) and Paper I that the steady-state enhancement V is given (in terms of the steady state intensities  $I_a^{SS}$  and  $I_b^{SS}$  of radicals a and b) as

$$V = \frac{(I_a^{SS} - I_b^{SS})}{(I_a^{SS} + I_b^{SS})} = \frac{P_a^{\circ} T_1 \beta}{\Im P_{\bullet \bullet} (1 + T_1 \beta \Delta P / \Im)} , \qquad (36)$$

where  $\beta = (k_0 \mathcal{F} k_2)^{1/2}$  is the experimentally observed second-order decay constant and  $k_0$  is the zero-order rate of production of radicals. [Equation (36) is obtained when one assumes radicals a and b are created at the same rate and react only by the spin-selective chemical reaction.] Note that by Eq. (32), etc., V is independent of  $r_i$ , the transferred radial separation, as it should be.

#### **III. RESULTS**

## A. Exchange Forces

Typical results for the exchange forces defined by Eqs. (4), (5), and (27), and k defined by Eq. (28) are given in Tables I-IV. We compare in Table I the results for  $P^{\circ}$ , F, and  $P^{\circ}/F$  both in the presence of the exchange forces (EFP) in the diffusion Eq. (4) and in their absence (EFA) (all other parameters remaining constant including the exchange terms in the spin Hamiltonian). This is done for a variety of values of  $J_0$  and k. One finds that  $\mathfrak{F}$ , the fraction which reacts, depends on k(and  $\Delta r$ ), but is independent of  $J_0$  for EFA. In the case of EFP, the results for F show a marked dependence on  $J_0$ , the larger the value of  $J_0$  the greater is F due to the enhanced effectiveness in trapping singlets at r=d, where they can react. Thus for small  $J_0 \leq 10^{11} \text{ sec}^{-1}$ , there is no difference between EFP and EFA in the values of F, but for  $J_0 \gtrsim 10^{13} \text{ sec}^{-1}$  the differences are quite marked. Another trend, which also emphasizes the increased trapping properties of EFP, is that for

		$D = 10^{-4}$ c	$\mathrm{cm}^2/\mathrm{sec}$	$D = 10^{-6}$	cm <sup>2</sup> /sec
$J_0(\sec^{-1})$	$k(\sec^{-1})$	$P^{\infty}  imes 10^3/ \mathfrak{F}$	Ŧ	$P^{\infty}  imes 10^3/ \mathfrak{F}$	F
1012	1014	11.5	0.458	36.0	0.574
$(0.025 \ kT)$	$10^{12}$	11.5	0.047	36.0	0.514
	10 <sup>10</sup>	11.0	$4.9 \times 10^{-4}$	35.9	$4.53 \times 10^{-2}$
	10 <sup>8</sup>	-31.0	$4.9 \times 10^{-6}$	30.0	$4.92 \times 10^{-4}$
$10^{13}$	1014	5.11	0.475	34.6	0.577
$(0.25 \ kT)$	$10^{12}$	5.06	$5.61 \times 10^{-2}$	34.6	0.529
	10 <sup>10</sup>	0.404	$6.29 \times 10^{-4}$	34.5	$5.68 \times 10^{-2}$
	$10^{8}$	-465	$6.3 \times 10^{-6}$	28.3	6.29 $\times 10^{-4}$
1014	1014	5.36	0,563	33.1	0.642
(2.5 kT)	$10^{12}$	5.36	0.291	33.1	0.635
	10 <sup>10</sup>	4.79	$5.90 \times 10^{-3}$	33.1	0.309
	<b>1</b> 0 <sup>8</sup>	-52.5	$5.96 \times 10^{-5}$	32.3	$5.91 \times 10^{-3}$
$4  imes 10^{14}$	10 <sup>14</sup>	5.35	0.631	32.3	0.719
$(10 \ kT)$	$10^{12}$	5.35	0.630	32.3	0.719
	10 <sup>10</sup>	5.35	0.606	32.3	0.719
	108	5.33	0.128	32.3	0.688
$1 \times 10^{15}$ (25 kT)	$10^8 - 10^{14}$	5.34	0.673	31.7	0.772

TABLE II. Effects of diffusion rate, in presence of exchange forces, on polarizations and spin-selective reaction.<sup>a,b</sup>

<sup>a</sup>All values are transferred results for  $r_t = d$ , cf. Eq. (32). Exchange forces are given by Eqs. (4), (5), and (27). k is defined by Eq. (28).

<sup>b</sup>Values of the other parameters are given in Table I.

 $J_0 \gtrsim 10^{13} \text{ sec}^{-1}$ , the disparity between EFP and EFA increases as k decreases. Thus, at  $J_0 \sim 10^{15} \text{ sec}^{-1}$ ,  $\mathfrak{F}$  is independent of k (for the values of k shown) for EFP, but is negligible for  $k \lesssim 10^{10} \text{ sec}^{-1}$  and EFA.

The results in Table I for EFA for  $P^{\infty}/\mathfrak{F}$  are found to be independent of k as already noted in Paper I [however, whereas in I, this independence had to be qualified as being for  $J_0 > 10^{10} \text{ sec}^{-1}$  (D  $10^{-5}$  cm<sup>2</sup>/sec), the present case does not require this, since as noted in Sec. II  $\rho_{S,T_0}$  is here not affected by k]. This is also generally the case for the larger values of  $J_0$  (and k) for EFP. In fact, in these cases the results for  $P^{\infty}/\mathfrak{F}$  are virtually identical for both EFP and EFA even when the respective values for F are markedly different (e.g., the cases of large  $J_0$  and  $k = 10^8 \text{ sec}^{-1}$ ). This important result demonstrates that, to a large extent, the polarizations are independent of the details of the spin-selective chemical reaction, and they are just linearly dependent on F. This, of course, means that in our models, where  $\hbar J_0/kT \gg 1$ , and the radical trapping (and reacting) region is around  $r \sim d$ , the region where polarization is developed lies where r > d such that  $\hbar J(r)/kT \ll 1$ . This is precisely the feature which is included in a simple manner in the EFA model as well as in I (where effects of k on  $\rho_{S,T_0}$  are differently treated). But the actual values of  $\mathfrak{F}$  and  $P^{\infty}$  are very model sensitive.

However, for the smaller values of  $J_0$  and k, the EFP and EFA results for  $P^{\infty}/\mathfrak{F}$  do not agree. In fact  $P^{\infty}/\mathfrak{F}$  and  $P^{\infty}$  for EFP change sign in some of the cases. This must be due to a new mechanism generating the polarization which no longer depends upon  $\mathfrak{F}$ . When  $\mathfrak{F}$  is negligible, then the small differences in Boltzmann factors for singlets vs triplets in the polarization region can have the effect of leading to a slight excess of singlets generating polarizations (this we call a relative diffusion model or RDM), which are negative in sign to effects of the reaction which depletes singlets. But for our model, the RDM polarizations are

TABLE III. Effects of range of exchange forces on polarization and spin-selective reaction.<sup>a,b</sup>

	$r_{\rm EX} = 2$ Å		$r_{EX} = 4$	Å
$J_0 \; (\text{sec}^{-1})$	$\overline{P^{\infty} imes 10^3/\Im}$	F	$\overline{P^{\infty}  imes 10^3/ \mathfrak{F}}$	Ŧ
1011	54.9	0.520	41.2	0.520
10 <sup>12</sup>	10.2	0.520	14.6	0.520
10 <sup>13</sup>	7.73	0.526	15.1	0.529
$10^{14}$	7.65	0.560	14.8	0.592
$4  imes 10^{14}$	7.60	0.594	14.7	0.659
$10^{15}$	7.58	0.616	14.6	0.705

<sup>a</sup>All values are transferred results for  $r_t = d$ , cf. Eq. (32). Exchange forces are given by Eqs. (4), (5), and (27).

<sup>b</sup>Values of the other parameters are given in Table II. The random initial condition is assumed.

			$\Delta F^{(c)}$		Φ(N, 1	$(d) \times 10^3$	
$s\Delta r^2/D$	$t \sim s^{-1} \sec$	$\hbar J_0 = 10 \ kT$	$\hbar J_0 = 25 \ kT$	EFA <sup>(e)</sup>	$J_0 = 4 \times 10^{14} \mathrm{sec}^{-1}$	$J_0 = 1 \times 10^{15} \mathrm{sec}^{-1}$	EFA
10-4	$2.5 \times 10^{-10}$	0.926	0.924	0.865			
10 <sup>-6</sup>	$2.5 \times 10^{-8}$	0,307	0.514	$2.87 \times 10^{-2}$	5.03	8.8	0
10-8	$2.5 \times 10^{-6}$	$6.99  imes 10^{-3}$	0.500	$2.93 \times 10^{-4}$	0.151	10.3	0
10-10	$2.5 \times 10^{-4}$	$7.09 \times 10^{-5}$	0.500		$-2.7 \times 10^{-3}$	10.3	0
$10^{-12}$	2.5×10 <sup>-2</sup>		0.460		$-4.3 \times 10^{-3}$	9.6	0
10-14	2.5		$5.14  imes 10^{-2}$		-4.3×10 <sup>-3</sup>	0.68	0
10 <sup>-16</sup>	$2.5 \times 10^{2}$		5.73 $\times 10^{-4}$		$-4.3 \times 10^{-3}$	-0.67	0

TABLE IV. Effectiveness of radical trapping for diffusion under spin-dependent exchange forces.<sup>a,b</sup>

<sup>a</sup>Exchange forces are given by Eqs. (4), (5), and (27).

<sup>b</sup>Values of other parameters used are: k=0,  $Q=1\times10^8$  sec<sup>-1</sup>,  $D=10^{-5}$  cm<sup>2</sup>/sec, d=4 Å,  $r_{\rm EX}=4$  Å,  $\Delta r=0.05$  Å, and random initial condition.

<sup>c</sup>Here  $\Delta F$  is the fraction of particles which have not reached the absorbing wall at  $r_N = 22$  Å. Also  $r_I = d = 4$  Å and f = 1.

<sup>d</sup>Polarizations at  $r_N = 212$  Å for  $r_I = 11.85$  Å. (Here M = 160, N = 360, and f = 20.)

<sup>e</sup>In the absence of exchange forces,  $\Delta F$  is independent of  $J_{0}$ .

much smaller than normal polarizations which arise from substantial values of  $\mathcal{F}$ .

In Table II we compare results for EFP for different diffusion rates. The general conclusions are unaffected, but one finds that (1) radical trapping and reacting is more effective for slower diffusion and (2) RDM polarizations are relatively more important (yielding very large values of  $P^{\infty}/\mathfrak{F}$ but still small values of  $P^{\infty}$ ) for faster diffusion.

In Table III we compare results for different values of  $r_{\text{EX}}$ . One continues to find  $P^{\infty}/\mathfrak{F}$  is the same for EFP and for EFA (the latter is not shown) for large k. However an increase in  $r_{\text{EX}}$  leads to an increase in  $\mathfrak{F}$ , because the ability to attract singlets into the reactive region is enhanced. This is *opposite* to the trend for EFA (cf. I), where an increase in  $r_{\text{EX}}$  leads to a decrease in  $\mathfrak{F}$  due to effects of S-T<sub>0</sub> mixing by the hyperfine interactions.

The results given in Tables I-III included the kinetically irreversible "reaction" at r = d to guarantee sensible behavior as the limit  $t \rightarrow \infty$  was taken (cf. Sec. II). We wished to test the results for our EFP model without the presence of this artifact, and this requires examining results for finite times. We have done this simply by using the well-known Fourier (and Laplace) inversion result that the behavior at time t is dominated by values of  $s \sim t^{-1}$  (and we checked this for the present type of calculation in I by direct inversion). We give in Table IV results showing the effectiveness of radical trapping for EFP when k = 0. We have compared the time it takes for radical pairs initially at r = d to collect at  $r_N = 22$  Å, a separation where exchange forces are negligible. The results for EFA are, of course, independent of  $J_0$ ; and for  $D = 10^{-5} \text{ cm}^2/\text{sec}$  used in Table IV 97% of the radi-

cals have collected by  $s^{-1} = 2.5 \times 10^{-8}$  sec. However, for EFP and  $\hbar J_0/kT = 10$  about 7% of the radicals have not reached  $r_N$  by 2.5×10<sup>-7</sup> sec, while for  $\hbar J_0/kT = 25$  all but 5% have reached  $r_N$  by  $s^{-1} = 2.5$ sec. The results for  $\hbar J_0/kT = 25$  show a plateau where nearly all the triplets have been collected by  $s^{\text{-1}} = 2.5 \times 10^{\text{-8}}$  sec but the singlets do not begin to be collected until  $s^{-1} = 2.5 \times 10^{-2}$  sec. We have also examined the time-evolved results for P(N) where  $r_N = 212$  Å in Table IV. For EFA we have P(N) = 0for all times, but for EFP large polarizations are built up for short times (while the singlets are still effectively trapped), but eventually the singlets reach  $r_N$  and neutralize the large polarizations except for the small RDM polarizations. It is interesting to note that for  $\hbar J_0 = 25 \ kT$ , the plateau value of  $P(N) = 10.3 \times 10^{-3}$  is precisely the result given in Table I which was obtained for  $k \neq 0$  and  $t \rightarrow \infty$  (for  $\hbar J_0 = 10 \ kT$ , there is no clean plateau region, so the comparison is not as clear). This kind of agreement supports our use of the artifact of the kinetically irreversible reaction at r = d to maintain the radical trapping. We note, however, that the lengths of time the singlets are trapped for EFP are surprisingly short considering the strengths of the trapping potential, which should lead to stable bond formation. This is undoubtedly due in part to the assumption of overdamping whereby momentum relaxation effectively occurs instantaneously.

Some comments apply to the calculation for  $\hbar J_0/kT = 25$ . It was not convenient to choose  $\Delta r$  small enough for this case, such that Eq. (20) was fulfilled for i=0 and the first several values of j. Thus, while some question exists as to the rigor of this particular calculation, we note that the results given in Tables I-IV show good consistency with

 $J_0(\sec^{-1})$  $J_0(d/\gamma) e^{-\lambda(r-d)}$  $J_0(r/d) e^{-\lambda(r-d)}$  $J_0(d/r)^{12}$  $J_0 e^{-\lambda(r-d)}$  $J_0(d/r)^6$ 0.359  $10^{8}$ 0.309 0.336 0.368 1.26  $10^{9}$ 3.09 3.358 3.678 12.453.59 1010 29.02 31.24 33.81 71.53 33.2  $10^{11}$ 41.91 40.33 38.67 61.74 41.2  $10^{12}$ 13.75 14.77 15.93 91.6 21.7  $10^{13}$ 27.3 14.39 15.18 16.01 1281014 14.25 14.93 15.62 16333.3  $10^{15}$ 40.3

TABLE V. Effects on polarizations of different functional dependences for J(r) with r.<sup>a,b</sup>

<sup>a</sup>Exchange forces are neglected in these calculations. The results are given for no chemical reaction, and the table entry is to be multiplied by  $\rho_{T_0T_0}(t=0) - \rho_{SS}(t=0)$ .

<sup>b</sup>Values of the other parameters used are:  $Q=1\times10^8$  sec<sup>-1</sup>,  $D=10^{-5}$  cm<sup>2</sup>/sec, d=4 Å,  $r_{\rm EX}=4$  Å,  $\Delta r=0.25$  Å (except for next to last column where  $\Delta r=2$  Å), M=32, N=72, f=20,  $r_N=212$  Å (but  $r_N=1664$  Å) for the last column and  $r_I=4$ Å.

all those results obtained for  $\hbar J_0/kT < 25$  where Eq. (20) was fulfilled for all j (and this is also true for calculations we have made for  $\hbar J_0/kT = 100$ . Most significant in this regard is the result of Table IV that  $\Delta F(N) \rightarrow 0$  as  $t \rightarrow \infty$  as it should. Also we have performed calculations where  $\Delta r = 0.25$  Å so that Eq. (20) was not completely fulfilled for  $\hbar J_0/kT = 10$ , but we obtained results very similar to those of Table I (for the larger values of k). (Note that for small k, the fact that k has been taken as nonzero only in the j = 0 "box" means that as  $\Delta r$  is changed, an exact comparison for small k values does not apply.) In principle, one may remove difficulties of this sort by extending our methods, whereby we have used two different values of  $\Delta r$ , to introduce a third, very small value for  $\Delta r$  in the region where  $\hbar J(r) > kT$ , etc.

## B. Functional Forms for J(r)

Given our results in I and above, that (1)  $P^{\infty}/\mathfrak{F}$ remains essentially constant for a wide range of descriptions of the spin selective reactive process and (2) an asymptotic value of  $P^{\infty}/\mathfrak{F}$  is obtained for large  $J_0$  (which is equal to  $P^{\infty}$  obtained for the triplet-initial case in the absence of any reaction), the question exists as to the sensitivity of this asymptotic result to the specific functional dependence of J(r) upon r. We have therefore considered as alternate forms:

$$J(\gamma) = (d/\gamma)^n J_0 e^{-\lambda (r-d)}$$
(37)

with n = -1, 0, and +1 as well as

$$J(r) = J_0 (d/r)^n \tag{38}$$

with n = 6 and 12. While exponential forms are expected for (medium range) exchange forces, we include the  $r^{-n}$  form for purposes of comparison, noting  $r^{-6}$  is characteristic of long-range van der Waals forces. Typical results for EFA are shown in Table V. One finds very similar results for all three exponential forms, including the existence of  $P_a^{\infty}$  (asympt) for large  $J_{0}$ . As *n* increases there is generally a rather small (and unimportant) increase in  $P_a^{\infty}$ . The  $r^{-6}$  form for J(r) behaves quite differently yielding generally higher values for  $P^{\infty}$ and showing no leveling off as  $J_0$  gets larger, although the  $r^{-12}$  form does show some leveling effects.

#### C. Ionic Interactions

We have, so far, only considered the case where Eq. (25) holds so that singlet and triplet spins experience equal, but opposite, valence forces. When the interactions are between charged radicals, then spin-independent Coulombic forces become important. We have studied this case, making use of the usual Debye formulas<sup>14,15</sup> for charge-shielding effects due to the ionic atmosphere in the solution. That is we have

$$U(\gamma) = \left(e^2 Z_a Z_b / \epsilon \gamma\right) \left[e^{-\kappa (r-d)} / (1 + \kappa d)\right] , \qquad (39)$$

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

$$\kappa^2 = (4\pi e^2/\epsilon kT) \sum_i n_i Z_i^2 \quad , \tag{40}$$

where  $\epsilon$  is the dielectric constant and  $n_i$  is the number density of the *i*th-type of particle of charge  $Z_i$ . We have obtained results for  $\kappa d \ge \frac{1}{4}$ , since the ionic atmosphere effects reduce the range of the interactions sufficiently for our computational convenience, and are typical of aqueous ionic solutions on which HE studies have been made, <sup>15</sup> i.e., a value of  $U(d) = 5kT/(1 + \kappa d)$  corresponding to  $d \sim 4$  Å, Z = 2, and  $\epsilon = 80$  and  $\frac{1}{4} \le \kappa d \le 2$  corresponding to

		Attra	ction	Rep	ulsion
$J_0(\sec^{-1})$	кd	$P^{\infty}/\mathfrak{F}$	Ŧ	$\overline{P^{\infty}}/\mathfrak{F}$	F
1010	<u>1</u>	108.2	1,587	1.14	0,0459
	$\frac{1}{2}$	110.3	1,235	1.86	0.0812
	1	104.4	0.918	3.96	0.166
	2	81.5	0.713	8.83	0.302
	No charge	31.2	0.527	31.2	0.527
1011	$\frac{1}{4}$	12.2	1.576	8.82	0.0459
	12	13.3	1.225	13.8	0.0812
	. 1	15.5	0.910	26.4	0.1657
	2	19.5	0.708	44.5	0.3017
	No charge	40.2	0.524	40.2	0.524
1012	14	5.01	1.575	9,63	0,0459
	$\frac{1}{2}$	5.47	1.225	13.7	0.0811
	1	6.43	0.910	20.1	0.166
	2	8.25	0.708	22.6	0.301
	No charge	14.7	0.524	14.7	0.524
10 <sup>13</sup>	$\frac{1}{4}$	6.71	1.572	12.2	0.0459
	12	7.32	1.223	16.3	0.0811
	1	8.61	0.909	20.6	0.166
	2	10.87	0.707	19.9	0.301
	No charge	15.1	0.523	15.1	0.523
1014	1	7.83	1,567	13.8	0.0459
	12	8.52	1.220	17.2	0.0811
	ĩ	9.96	0.907	19.4	0.1654
	2	12.2	0.706	17.7	0.3007
	No charge	14.8	0.522	14.8	0.522

TABLE VI. Effects of Coulombic interactions on polarizations and spin-selective reaction.  $^{a,b}$ 

<sup>a</sup>Spin-independent Coulombic interactions are given by Eqs. (34), (40), and (5), and  $U(d) = 5kT/[1 + \kappa d]$ .

<sup>b</sup>Values of the other parameters used are  $k = 10^{14}$  sec<sup>-1</sup>,  $Q = 1 \times 10^8$  sec<sup>-1</sup>,  $D = 10^{-5}$  cm<sup>2</sup>/sec,  $d = r_{EX} = 4$  Å,  $\Delta r = 0.25$  Å, N = 168, M = 128, f = 20,  $r_N = 236$  Å;  $r_I = 34$  Å.

~ 0.01M to greater than 0.25M in ionic (Z=2) concentration were used, even though the quantitative validity of Eq. (39) is uncertain for such high concentrations. Typical results for EFA are summarized in Table VI. It is clear that attractive forces significantly aid the reaction, essentially by extending its range, and the longer the range of the attractive forces (less ionic screening) the more effective it is. [The values of  $\mathcal{F}(d_t)$  significantly greater than  $\frac{1}{2}$  reflect this increased range, and not any reaction of triplets. ] The behavior of  $P^{\infty}/\mathfrak{F}$ is not as simple. For attraction where  $D \sim 10^{-5}$  $cm^2/sec$  and  $J_0 < 10^{11} sec^{-1}$  (or more generally  $J_0\tau_1 < 1$ )  $P^{\circ}/\mathfrak{F}$  rapidly increases with decreasing  $\kappa d$ , representing the fact that radicals are more readily attracted to r = d (and retained there) where the dominant polarization may occur. But for  $D \sim 10^{-5}$ cm<sup>2</sup>/sec and  $J_0 > 10^{11}$  sec<sup>-1</sup> (or more generally  $J_0 \tau_1$ > 1),  $P^{\infty}/\mathfrak{F}$  decreases as  $\kappa d$  decreases (although the effects appear small), since the region of effective polarization occurs where r > d, while spin depolarization is very effective for  $r \approx d$ , the region to which the radicals are attracted. Generally, opposite trends are observed when the Coulombic forces are repulsive (except for  $\kappa d < 1$ ). The reason why the Coulombic forces can result in changes in  $P^{\infty}/\mathfrak{F}$ , while the inclusion of exchange forces had

no such effects, may be attributed to the fact that even when  $\hbar J_0/kT > 1$ , the range of r where there is effective polarization always obeys  $\hbar J(r)/kT \ll 1$ , but the more long-range Coulombic forces can still fulfill  $U(r)/kT \ge 1$  in this range of r/.

## D. Quenching of Initial Polarization

We give in Tables VII and VIII typical results for the effects of quenching of initial polarization. We have utilized EFA since (1) the off-diagonal elements  $\rho_{S,T0}$ , which are the important terms here, are unaffected by the exchange forces and (2) the depolarization should occur in regions of  $J_0 \sim D/d^2$  $\ll kT/\hbar$ . The results for a contact exchange model, where  $J(r_j)=J_0\delta_{r_j,r_0}$  appear in Table VII, and may be summarized by

$$\Delta P(d_t) \cong \left\{ (2J_0\tau_1)^2 / [1 + 4(J_0^2 + Q^2)\tau_1^2] \right\} \\ \times \left[ 1 - H(Qd^2/D, J_0d^2/D) \right] , \quad (41)$$

where

$$\tau_1 \cong V(0)/D = d\Delta r/2D \quad . \tag{42}$$

Equation (42) is the same "lifetime for the encounter pair" that was found for the behavior of  $P_a^{\infty}$  for the contact-exchange model.<sup>1</sup> Also, when  $H(Qd^2/D, Jd^2/D) = 0$ , then Eq. (41) gives just the probability of Heisenberg spin exchange per  $(S - T_0)$  encounter that has been determined from relatively simple analytical solutions.<sup>16,17</sup> We have found that

$$H(Qd^2/D, \ J_0d^2/D) \cong \frac{h(Qd^2/D)}{\left[1 + 4(J_0^2 + Q^2)\tau_1^2\right]}$$
(43)

such that H is typically small compared to unity, but it has an approximately nearly linear dependence upon  $Qd^2/D$  (for  $D \sim 10^{-5}$  and  $Q \sim 10^{+8}$ ).<sup>18</sup> This extra term, represents the effect of successive re-encounters, which tend to generate new polarizations, an effect which was not included in these earlier models.

Typical results for finite range of the exchange are given in Table VIII. The most significant difference from a contact exchange model is that for large  $J_0 \gtrsim 10^{11} \sec^{-1}$  (and typical values of D and  $r_{\rm EX}$ , or alternatively  $J_0\tau_1 > 1$  see below) it is possible to have  $\Delta P(d_t) > 1$  representing the fact that the depolarization is completed at radical separations > d. For these large  $J_0$  values, the results in Table VIII indicate that  $\Delta P(d_t)$  varies roughly as  $\sqrt{r_{\rm EX}/d}$  with only a small (positive) dependence on  $Jd^2/D$  (and a virtually negligible dependence on  $Qd^2/D$ ). For small  $J_0$  (more precisely  $J_0\tau_1 < 1$ with  $\tau_1$  defined below) one has a result very similar to Eq. (41):

$$\Delta P(d_t) \simeq (2J_0\tau_1)^2 [1 - H'(Qd^2/D, J_0d^2/D)] \quad , \quad (44)$$

where

	1	$Q=10^8$ , $\Delta r=1$ Å	3	$D = 10^{-5} \text{ cm}^2/\text{s}$	sec, $\Delta r = 1 \text{ Å}$	6 $D = 10^{-5} \text{ cm}^2/\text{sec}$
$J_0(\sec^{-1})$	$D = 10^{-4} \mathrm{cm}^2/\mathrm{sec}$	$D = 10^{-5}  \mathrm{cm}^2 / \mathrm{sec}$	$D = 10^{-6}  \mathrm{cm}^2 / \mathrm{sec}$	$Q = 0.1 \times 10^8  \mathrm{sec}^{-1}$	$Q = 10 \times 10^8 \text{ sec}^{-1}$	$\Delta r = \frac{1}{4} \text{ Å}$
108	$1.51 \times 10^{-7}$	1.38×10 <sup>-5</sup>	1.02×10 <sup>-3</sup>	$1.51 \times 10^{-5}$	1.02×10 <sup>-5</sup>	$0.860 \times 10^{-6}$
$10^{9}$	$1.51 \times 10^{-5}$	$1.37 \times 10^{-3}$	$0.926 \times 10^{-1}$	$1.51 \times 10^{-3}$	1.02×10 <sup>-3</sup>	$0.860 \times 10^{-4}$
$10^{10}$	$1.51 \times 10^{-3}$	0.121	0.911	0.131	$0.926 \times 10^{-1}$	$0.853 \times 10^{-2}$
$10^{11}$	0.131	0,932	0.999	0.938	0.911	0.462
$10^{12}$	0.938	0,999	1.000	0.999	0.999	0.989
$10^{13}$	0.999	1.000	1.000	1.000	1.000	1,000
1014	1.000	1.000	1.000	1.000	1.000	1.000

TABLE VII. Polarization quenching by a contact exchange mechanism. a-c

<sup>a</sup>The table entries give  $\Delta P(d)$ .

<sup>b</sup>Values of parameters as indicated by column headings. Other parameters used are: d=4 Å, M=10, N=30, f=10,  $r_N=213$  Å.

<sup>c</sup>Note that by scaling most of Column 4 may be obtained from Column 1, and similarly for Columns 3 and 5.

$$\tau_1 \cong d/D\lambda \cong 0.1 r_{\rm EX} d/D \tag{45}$$

and H' is very similar to H. The form, Eq. (45), was also obtained in I in analyzing results for  $P_a^{\infty}$  for small  $J_{0}$ .

#### E. Nonspherical Radicals

All our calculations have been performed for spherically symmetric exchange interactions and spherical radicals for reasons of simplicity. Since most interacting radicals will display anisotropic features in their exchange interactions and their ability to react, some comments on expected effects from nonspherical features are appropriate.

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

though they each represented the behavior of a different spherical molecule). (Also, we are neglecting any effects from the orientation dependence of d and  $r_{\rm EX}$  on  $Qd^2/D$  and  $r_{\rm EX}/d$  in our discussion.)

The main points to note now are (1)  $P^{\infty}/\mathfrak{F}$  is independent of  $\mathfrak{F}$  for spherical radicals; (2) for a nonspherical radical,  $\mathfrak{F}$  may be greatly reduced by a geometric factor, but if contours around the mol-



FIG. 2. Nonspherical radicals. (a) Suggested contours of constant J value about a nonspherical radical interacting with a spherical radical. Spin-selective chemical reaction may occur only at Region 1. (b) Typical variation of  $P^{\infty}/\mathfrak{F}$  with  $J_0 d^2/D$  for spherical radicals showing suggested equivalent points corresponding to Regions 1-4 in (a) (cf. text).

		IADL	E VIII. Polariza	thoir quenching t	by exchange filter				
		$Q = 10^{7};$	$r_{\rm EX} =$	A. Depend	ence on $r_{\rm EX}$ <sup>b</sup>	$J_0 =$	$10^8$ ; $r_{\rm EX} =$		
	$J_0(\sec^{-1})$	2 Å	4 Å	8 Å	- Q×10	-8 2 Å <sup>c</sup>	4 Å <sup>c</sup>	8 Å <sup>c</sup>	
	108	2.61×10 <sup>-6</sup>	9.40×10 <sup>-6</sup>	$4.53 \times 10^{\circ}$	-5 0.2	2.58	9.27	44.5	
	10 <sup>9</sup>	2.61×10 <sup>-4</sup>	$9.40 \times 10^{-4}$	$4.52 \times 10^{\circ}$	-3 0.4	2.52	8.99	42.9	
	10 <sup>10</sup>	$2.56 \times 10^{-2}$	$8.68  imes 10^{-2}$	0.335	0.6	2.45	8.76	41.7	
	1011	0.754	1.015	1.271	1.0	2.38	8.46	40.1	
	$10^{12}$	1.059	1.188	1,633	2.0	2.24	7.93	37.1	
	10 <sup>13</sup>	1.135	1.399	2.072	4.0	2.06	7.23	33.4	
	1014	1.241	1.615	2.525	6.0	1.94	6.74	30.7	
			в.	Dependence on	Other Paramet	ers <sup>d</sup>			
		$D = 10^{-4}; Q =$			$D = 10^{-5}; Q =$			$D = 10^{-6}; Q =$	
$J_0(sec^{-1})$	107	108	109	107	108	109	107	108	10 <sup>9</sup>
108	9.44×10 <sup>-8</sup>	9.40×10 <sup>-8</sup>	8.46×10 <sup>-8</sup>	9.40×10-6	8.46×10-6	$6.04 \times 10^{-6}$	8.46×10-4	6.04×10 <sup>-4</sup>	2.53×10 <sup>-4</sup>
10 <sup>9</sup>	$9.44 \times 10^{-6}$	$9.40 \times 10^{-6}$	$8.46 \times 10^{-6}$	$9.40 \times 10^{-4}$	$8.46 \times 10^{-4}$	$6.04 \times 10^{-4}$	$7.87 \times 10^{-2}$	$5.74 \times 10^{-2}$	$2.47 \times 10^{-2}$
10 <sup>10</sup>	$9.44 \times 10^{-4}$	$9.40 \times 10^{-4}$	$8.46 \times 10^{-4}$	$8.68 \times 10^{-2}$	$7.87 \times 10^{-2}$	$5.74 \times 10^{-2}$	1.002	0.955	0.775
10 <sup>11</sup>	$8.72 \times 10^{-2}$	$8.68 \times 10^{-2}$	$7.87 \times 10^{-2}$	1.015	1,002	0.955	1.186	1.179	1,153
10 <sup>12</sup>	1.016	1.015	1.002	1.188	1.186	1.179	1.398	1.389	1.360
10 <sup>13</sup>	1,188	1.188	1,186	1,399	1.398	1.389	1.613	1.604	1.574
1014	1.399	1.399	1,398	1.615	1.613	1.604	1.831	1.822	1.791

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<sup>a</sup>The table entries give  $\Delta P(d_t)$ .

<sup>b</sup>Values of other parameters are  $D = 10^{-5}$  cm<sup>2</sup>/sec, d = 4 Å,  $\Delta r = \frac{1}{4}$  Å ( $\frac{1}{2}$  Å for  $r_{\text{EX}} = 8$  Å), N = 72, M = 32, f = 10 (5 for  $r_{\text{EX}} = 8$  Å)  $r_N = 112$  Å (119 Å for  $r_{\text{EX}} = 8$  Å),  $r_I = 11.5$  Å (19 Å for  $r_{\text{EX}} = 8$  Å).

<sup>c</sup>Entries are  $\Delta P(d_t) \times 10^6$ .

<sup>d</sup>Values of parameters as indicated by column headings. Other parameters used are:  $r_{EX} = 4$  Å, d = 4 Å,  $\Delta r = \frac{1}{4}$  Å, N = 72, M = 32, f = 10,  $r_f = 11.5$  Å,  $r_N = 112$ Å.

ecule include Regions 1-4, then the polarization that is achieved is still of the order of magnitude of  $P^{\infty}$  (asympt)/ $\mathfrak{F}$  as calculated for spherical molecules; (3) since (in most cases) all the polarization depends on the value of  $\mathfrak{F}$  originally generated, then we still have the resulting  $P^{\infty}/\mathfrak{F}$  independent of  $\mathfrak{F}$ . This value of  $P^{\infty}/\mathfrak{F}$  will probably lie somewhere between  $P^{\infty}(\max)/\mathfrak{F}$  and  $P(\operatorname{asympt})/\mathfrak{F}$  for many cases, [e.g.,  $P(\operatorname{asympt})/\mathfrak{F}$  for nearly spherical molecules or approximately  $P^{\infty}(\max)/\mathfrak{F}$  if regions like 2 and 3 dominate].

## F. Comparison with Experiment

Fessenden<sup>19</sup> has reported results for the radicals  $\dot{C}H_2COO^-$ ,  $\dot{C}H(CO_2^-)_2$ , and  $\dot{C}_6H_6OH$ , which correspond to values 2 or 3 times those we have estimated for  $P^{\infty}(asympt)/\Im$  for spherical radicals, but *not* greater than  $P^{\infty}(max)/\Im$ , so it is possible that the above arguments apply. In fact they would lead to a most probable (or average)  $J_0 \sim 10^{10}-10^{11}$  sec<sup>-1</sup>.

Verma and Fessenden<sup>20</sup> have recently obtained polarization results for hydrogen radicals. Here, since we are dealing with spherical atoms, the experimental  $P^{\infty}/\mathfrak{F}$  of ~  $50 \times 10^{-3}$  should equal  $P^{\infty}(asympt)/\mathfrak{F}$ . If we take as nominal values of  $d \sim 1$  Å,  $r_{EX} \sim 4$  Å,<sup>12</sup> then we get for D=1, 2, and  $5 \times 10^{-5}$  values of  $P^{\infty}(asympt)/\mathfrak{F}$  60, 49, and  $34 \times 10^{-3}$ or rather good agreement (with only a weak dependence on d and a nearly linear dependence on  $r_{EX}$ ).

We might also comment at this point on the charge repulsion and ionic strength effects in Fessenden's experiments. Thus, he observes significantly lower enhancements for 0.01M concentrations of CH<sub>3</sub>CO<sub>2</sub> (forming CH<sub>2</sub>CO<sub>2</sub>) than for 0.1*M*. Also  $\dot{C}H(CO_2)_2$  yields smaller enhancements than  $\dot{C}H_2(CO_2)$ . This could be explained if the nonspherical radicals are dominated by  $J_0 < J_{max}$  (i.e., Regions 2 and 3 of Fig. 2), for which repulsion decreases  $P^{\infty}/\mathfrak{F}$  and this decrease is more pronounced for smaller  $\kappa d$  (i.e., lower ionic strength). (Note that one must be careful to distinguish between the observed enhancement V given by Eq. (36) and the polarization  $P^{\infty}/\mathfrak{F}$ ). Recent experiments by Livingston<sup>21</sup> also suggest the importance of ionic concentrations.

#### **IV. SUMMARY**

#### A. This Work

The main result of this work, in which we explicitly considered the effects of valence forces on diffusion and CIDEP intensities, is the demonstration that the quantity  $P_a^{\omega}/\Im$ , the polarization generated per fractional probability that singlets react, remains virtually independent of the actual

details of the spin-selective-reactive process. This is justified by noting that the actual reaction occurs only for values of r for which  $\hbar J(r)/kT \gtrsim 1$ , while the significant contributions to the polarization occur for larger values of r such that  $\hbar J(r)/kT < 1$ . This implies the adequacy of the simple model used in Paper I in which a simple spin-selective reaction is allowed to occur just at the internuclear separation d except that the present work suggests that such a spin-selective chemical process does not directly induce CIDEP depolarization; thus the EFA model in this work would be more satisfactory. [This latter result may well be important for nonspherically symmetric radical-pair interactions, enabling the possibility of generating values for  $P_a^{\infty}/\mathfrak{F} > P_a^{\infty}(asympt)/$ F, cf. Fig. 2(b).] As one would expect, however, the actual magnitudes of  $P_a^{\infty}$  and  $\mathfrak{F}$  are sensitive to the details of the reactive processes, and one example is that for the present EFP model, an increase in the range of J(r) leads to an increase in F, just the opposite of that found in I. Yet in many experiments, it is sufficient to know just  $P_a^{\infty}/\mathfrak{F}$ . Our values of  $P_{\mathbf{a}}^{\infty}/\mathfrak{F}$  for reacting H atoms [for which J(r) is spherically symmetric] appear to agree well with the experimental results of Verma and Fessenden.<sup>20</sup>

We have found that while the differences in the diffusive trajectories for singlets vs triplets can lead to a net polarization, such effects are generally overwhelmed in our model by the reactive process itself when  $\mathcal{F}$  is not negligible.

On the other hand, Coulomb interactions between charged radicals, which are more longrange, can indeed have significant effects on  $P_a^{\infty}/\mathfrak{F}$ , and the trends are different depending on whether  $J_0$  is large or small. Such trends as a function of ionic concentrations could be useful indicators of the details of the polarization process and some recent experimental results are discussed in this light.

Our earlier result, that  $P_{\mathbf{a}}^{\infty}/\mathfrak{F}$  achieves an asymptotic value for large  $J_0$ , has been shown to be true for several forms of J(r) which are primarily exponentially decaying in r with the actual values of  $P_{\mathbf{a}}^{\infty}/\mathfrak{F}$  rather insensitive to these forms. But an  $r^{-6}$ -type dependence does not level off asymptotically for large (but reasonable) values of  $J_0$ .

Our results on spin depolarization by Heisenberg spin-exchange between randomly colliding radical pairs are, for a contact-exchange model, similar to earlier results on Heisenberg-spin exchange except that (1)  $\tau_1$  the "lifetime" of the radical pair is more precisely defined and (2) effects from successive re-encounters in the collision are obtained. For J(r) of finite extent, however, the effective radial range of depolarization increases roughly as  $\sqrt{r_{\text{EX}}}$  for large  $J_0$  with only a weak dependence on  $J_0/D$  for the reasonable values of parameters investigated. For these values, the effective range changes by a factor of order 1 to 2.5 from the contact-exchange value of d.

## B. Comparison with Other Work

We note that earlier attempts (through 1971) to analyze CIDEP in terms of a radical-pair mechanism have recently been reviewed, 22 and we have already pointed out<sup>1,2</sup> that these were based on simplified submodels of the complete dynamics, while the stochastic-Liouville method includes the appropriate ensemble average over all the trajectories for the diffusive motion. It was shown in Paper I, that our analysis supports Adrian's<sup>23</sup> original idea of the important role played by radical-radical re-encounters for normal diffusion rates  $(D \sim 10^{-5} \text{ cm}^2/\text{sec})$ , but the description must be modified for significantly faster or slower motion. Adrian has very recently<sup>24</sup> presented an approximate calculation of CIDEP magnitudes (for large  $J_0$  only) which explicitly incorporates the re-encounter concept, but it is limited by his treatment of the effects of J(r) in terms of only a first-order perturbation, while dealing with the spatial region of large J(r)in an ad hoc fashion. Our exact numerical results in I and this work are again consistent with Adrian's<sup>24</sup> qualitative model when  $D \sim 10^{-5} \text{ cm}^2/\text{sec}$ , but, although his results for large  $J_0$  are of comparable order of magnitude, they do not display the kind of functional dependences found in our work, presumably due to his simplifying assumptions. Evans et al.<sup>25</sup> have very recently attempted an analytical solution to the stochastic-Liouville equation given

in Ref. 1, for a simplified and approximate model. That is, they attempt to approximate the effects of an exchange interaction of finite extent as a Diracdelta function with the same volume integral. Their result bears just a qualitative similarity to our contact-exchange model given in I (as well as an earlier form reviewed in Ref. 22). We, have, however, already pointed out in I, that the predictions for the more realistic models which include the finite range of J(r), are qualitatively different from contact-exchange models (including the model of Evans et al.). The former yield substantial polarizations, asymptotically independent of  $J_0$ . Evans et al. introduce a selective chemical reaction also with a delta function range and at the same internuclear distance as J(r). The models including exchange forces given in this present work clearly show that the chemical reaction should properly occur at closer internuclear distances than the CIDEP polarization effects of J(r)as we have discussed above, This leads to qualitatively different dependence of CIDEP on the rate constant for our models with finite range of J(r)(as well as Adrian's work) vs the delta function approach of Evans et al. (Another apparent weakness in their work is their neglect of a distance of closest approach in the relative diffusive motion. The radicals are thus free to move *into* one another.)

While all the previous work (including I) treated the relative motion as simple, unhindered Brownian motion, it is only in the present work that effects of attractions and repulsions (both spin dependent and independent) have been considered in an effort to deal with more realistic models. The stochastic-Liouville approach is quite general, and one may expect to see more complete descriptions of the dynamics in the future.<sup>26</sup>

## APPENDIX: GLOSSARY OF MAIN SYMBOLS

$d = r_0$	Distance of closest approach of the radical pair (i.e., contact distance)
$D = D_{a} + D_{b}$	Diffusion coefficient for relative motion of radical pair
$\mathbf{D}\Gamma_{\mathbf{r}}, D\Gamma_{\mathbf{r}}$	Diffusion operator for relative diffusion of radical pair
$D\mathbf{W}$	Finite-difference transition matrix for diffusion
$eZ_i$	Charge on <i>i</i> th molecule
$\boldsymbol{\hat{F}}(\boldsymbol{\gamma}) = (\boldsymbol{\gamma}/kT) \big[ \partial U(\boldsymbol{\gamma})/\partial \boldsymbol{\gamma} \big]$	Dimensionless force of interaction between radical pair, $F(r) = r^{-1} \hat{F}(r)$
F, F(N)	Probability of reaction for the radical pair per collision
$\mathfrak{K}^{\times}(\mathbf{r}_{i})$	Liouville operator for the radical pair, associated with the spin Hamiltonian $\mathfrak{K}(\mathbf{r}_i)$
$I_{\rm a}, I_{\rm b}$	CIDEP intensities for radicals a and b
$I_{a}^{SS}$ , $I_{b}^{SS}$	Steady-state values of $I_a$ and $I_b$
$J(\mathbf{r}_{a}, \mathbf{r}_{b}), J(\gamma)$	Exchange interaction between radical pair

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$J_0 \equiv J(\gamma = d)$	Note $J_{\max}$ is the value of $J_0$ which gives the maximum value of $P^{\bullet}/\mathfrak{F}$ .
k	First-order rate constant for irreversible disappearance of singlet radical pairs when in contact
$k_0$	Zero-order rate of production of radicals (e.g., due to a light beam)
$k_2(r_I), \ k_2(d)$	One-half the second-order rate constant for new bimolecular collisions at separation $r_I$ or $d$
$n_{a}(t), n_{b}(t)$	Number density of radicals a and b
$P_{\mathbf{a}}(t), \ P_{\mathbf{a}}^{\infty} \ (\text{or} \ P^{\infty})$	Polarization of radical a at time $t$ and at infinity
$P_{a}^{\infty}(r_{I}), P_{a}^{\infty}(r_{t})$	$P_{\rm a}^{\infty}$ generated from an initial separation for the radical pair of $r_I$ , or transferred according to Eq. (32) to $r_t$
$\Delta P(r_I), \ \Delta P(r_t)$	The fractional change in the polarization from that which exists at the onset of the collision
$\mathcal{P} \equiv 1 - \mathfrak{F}$	Probability a radical pair does not react per collision
$p(\mathbf{r})$	Classical distribution function for relative motion of the radical pair
Q	Half the difference in ESR resonant frequencies of the two interacting radicals
$r_0 \equiv d$	Distance of closest approach of the radical pair
$\gamma_{\rm EX} = \lambda^{-1} 5 \ln 10$	
Υ <sub>I</sub>	Separation of radical pair at the initiation of a collision
Υ <sub>M</sub>	Separation distance such that $J(r > r_M)$ and $U(r > r_M)$ are zero
$\gamma_N$	Position of outer absorbing wall
$\Delta r; f \Delta r$	Radial increments for finite differences
S	Singlet state
T <sub>0</sub>	Triplet, $M = 0$ state
T <sub>1</sub>	Longitudinal spin-relaxation time
U(r)	Potential energy of interaction between the radical pair, which can be spin dependent [e.g., $U_{SS}(r)$ is potential for singlet radical pairs]
V(i)	Radial weighting factor for $r_i$ th position for finite differences
$\beta \! \equiv (k_0 \! \mathfrak{F} k_2)^{1/2}$	Experimentally observed second-order decay constant
E	Dielectric constant of solvent
κ	Debye's reciprocal thickness of the ionic layer
λ	Exponential decay constant in r for $J(r)$
$\rho(\mathbf{r}_i, t), \ \rho(r, t)$	Spin-density matrix for radical pair; $\hat{\rho}(r, t) = r\rho(r, t)$
$\rho_0(r) \equiv \rho(r, 0)$	
$\rho(t)$	Space average of $\rho(\mathbf{r}_i, t)$
$ au_1$	Lifetime for the encounter pair
Ω	Finite-difference matrix of the elements of $\mathfrak{K}^{x}(\mathbf{r}_{i})$
EFP(EFA)	Model with exchange forces present (absent) in the diffusion equation
RDM	Relative diffusion model; an EFP model where radical pairs are not permanently bound

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- <sup>4</sup>R. Kubo, Adv. Chem. Phys. 16, 101 (1969); J. Phys. Soc. Jap. Suppl. 26, 1 (1969).
- <sup>5</sup>Ideally one would expect from a "complete" theory that the density matrix would relax to the thermal equilibrium value  $\rho_{eq} = \exp(-\hbar \Re/kT)/\operatorname{Tr} [\exp(-\hbar \Re/kT)]$ . The form of Eq. (13) suggests that the relaxation tends to  $p'_{eq}$  $= \exp(-(\hbar \mathcal{H}_0/kT)/\mathrm{Tr}[\exp(-\hbar \mathcal{H}_0/kT)] \text{ where } \mathcal{H}_0 \text{ of Eq. (2)}$ includes both the (average) Zeeman terms  $\mathcal{K}_{0,z}$  (cf. I) and the exchange interaction  $\mathcal{K}_{0,J}$ . More precisely the  $\hat{\Gamma}_{i}$  just relaxes each matrix element  $\rho_{ij}$  for  $i, j=S, T_0$ with respect to radial position according to  $\mathcal{R}_{0,J}$ . At least two other types of condition are needed to get relaxation to  $\zeta'_{eq}$ : (1) Interconversion between S and  $T_0$ induced by  $\mathcal{K}'$ , where such interconversion is important only in the spatial regions for which  $\hbar J(r)/kT$  (since  $\hbar \mathcal{H}'/kT \ll 1$ ; and (2) since  $[\mathcal{H}_{0,J}, \mathcal{H}_{0,z}] = [\Gamma_r, \mathcal{H}_{0,z}] = 0$ , it is only necessary to add then a regular  $T_1$  mechanism. However, because  $[\mathcal{H}_{0,J}, \mathcal{H}'] \neq 0$  one cannot readily modify our expressions to get relaxation to  $\rho_{eq}$ . The problem arises because  $\Gamma_r$  is written in a basis which does not diagonalize  $\mathfrak{K}'$ , i.e., the quantum nature of the back reaction of the "lattice" on the spins is not fully included. In the present case where  $\mathcal{K}' \ll \mathcal{H}_{0,z}, J_0, kT/\hbar$ this problem is not important.
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- <sup>8</sup>This statement can be analyzed from the point of view of a simple "two-site" model involving a single spin S of  $\frac{1}{2}$  jumping between two sites A and B such that for  $|\pm\rangle_A + |\pm\rangle_B$  the jump rate, when neglecting Boltzmann factors, is independent of spin. If a simple relaxation matrix treatment is given (cf. Ref. 6) involving the matrix element for the transition from A to B, one finds that  $R_{+A-A}, +_{B-B} = \frac{1}{2}(W_{+B++A} + W_{-B--A}), R_{+A-A}, +_{A-A}$  $= -\frac{1}{2}(W_{+A-+B} + W_{-A--B})$ , where  $R_{\alpha\alpha'},_{\beta\beta'}$  is a relaxation matrix element and  $W_{\pm A+\pm B}$  is the transition probability from  $\pm A$  to  $\pm B$  etc. (properly including Boltzman factors). Our use of  $\Gamma_r$  is seen to be a generalization of this to a continuous range of sites.
- <sup>9</sup>Note that, while we are not explicitly including any  $T_1$  process during the collision, a more complete analysis would allow for  $T \rightarrow S$  relaxation when the radicals are strongly interacting (i.e., at  $r \sim d$ ). Then this would have the effect of reducing somewhat the spin selectivity of the reactive process.  $\mathcal{F}$ , as defined by Eq. (24), would no longer simply correspond to the value of  $\rho_{T_0T_0} \rho_{SS}$  after the reaction (to which the polarization generated will be proportional), but is easily modified for this purpose. One could, in an ad hoc fashion, introduce transition probabilities  $W_{S + T_0}(r)$  and  $W_{T_0 + S}(r)$ , with an appropriate "range of influence" in r, into Eq. (13), such that  $W_{S + T_0}(r)/W_{T_0 + S}(r) = \exp(2\hbar J/kT)$ . Also the diagonal elements for  $\rho_{ST}$  and  $\rho_{TS}$  should have added to them:  $(\frac{1}{2})(W_{S + T} + W_{T + S})$  with off-diagonal elements

between  $\rho_{ST}$  and  $\rho_{TS}$  equal to minus these diagonal elements. Such an analysis is necessarily incomplete because of the neglect of the  $T_{\pm 1}$  states and their role in the spin relaxation.

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- <sup>26</sup>E. g., J. M. Deutch, J. Chem. Phys. (to be published) has recently pointed out how one may introduce the hydrodynamic effects of the interacting flow patterns of the free radicals into the CIDEP problem. We are currently applying our finite-difference methods of the present work to obtain the detailed solutions as suggested by Deutch.