

A hydrodynamic effect on chemically induced dynamic spin polarization*

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Deutch has recently suggested that the effect of the hydrodynamic interaction represented by Oseen's tensor, on the relative diffusion of radical pairs, should have consequences for CIDNP and CIDEP signals. Detailed solutions to this problem have now been obtained by the finite difference approach of Pedersen and Freed to the stochastic-Liouville equation for the radical-pair mechanism. These solutions show that the hydrodynamic interaction typically leads to polarizations enhanced by factors of the order of 0.9–3 for CIDEP and reduced by factors of (3/4)–2(1/2) for the appropriate CIDNP parameter, and these factors are a function of the nature and magnitudes of the various interactions.

I. INTRODUCTION

Deutch¹ has recently drawn attention to a hydrodynamic interaction that influences the relative diffusive motion of a radical pair. It should therefore affect CIDNP and CIDEP phenomena, since they are particularly sensitive to the relative diffusive motion.

One must emphasize at the outset that the CIDNP and CIDEP phenomena are, in general, sensitive to *all* aspects of the details of the relative dynamical motions and interaction potentials of the radical pair. The ultimate better understanding of these interesting experiments and how to devise more meaningful experiments will rest, to some extent, on a theoretical understanding of these aspects. It has been our objective, in earlier treatments^{2–5} (I, II, III) of these phenomena, to illustrate with simple, though meaningful, physical models the potential relevance of features of the molecular dynamics and interactions to the CIDNP and CIDEP observables. Thus, in the earlier work, we have considered the effects of the magnitudes and functional forms of the exchange interaction^{3,4}; we have considered the effects of intermolecular interactions on the relative diffusion of the radical pair both in terms of the spin-dependent exchange interactions and also the spin-independent Coulombic interactions in the Debye–Hückel fashion.^{4,5} In particular, we found that the long-range Coulombic interactions could cause rather dramatic changes of both the electron and nuclear spin polarizations, while the short range exchange effects on the diffusion tended only to have small effects on the experimentally relevant polarization quantities. There are many ways in which one may wish to improve the theoretical models beyond these corrections to the simple picture of relative diffusion of spherical molecules. Thus, for example, the relative molecular diffusion under strong reactive potentials should properly include inertial-effect corrections, and for most molecules, the exchange interaction $J(\mathbf{r})$ must be highly orientation dependent and not spherically symmetric. Furthermore, one would like to incorporate into both the statics and dynamics of the model more details about the structure of the liquid in the form of a good pair correlation function. All these relevant improvements can be successfully incorporated into our method of analysis, and we plan to report on such studies in the future.

For the present short work we have chosen to consider Deutch's suggestion.¹ This hydrodynamic interaction between Brownian particles in a liquid results from the fact that each particle creates a systematic flow pattern which affects the flow of the other particles. This hydrodynamic effect is approximately taken into account for spherical Brownian particles by using a modified diffusion operator^{6,7}:

$$\Gamma_{\mathbf{r}} = \nabla \cdot [D\mathbf{1} - 2(kT)\mathbf{T}(\mathbf{r})] \cdot \{\nabla + (kT)^{-1}[\nabla U(\mathbf{r})]\}, \quad (1.1)$$

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

$$\mathbf{T}(\mathbf{r}) = (8\pi\eta r)^{-1} [\mathbf{1} + \mathbf{r}\mathbf{r}(r^{-2})], \quad (1.2)$$

with η the solvent viscosity, D the diffusion coefficient for the relative motion between the two radicals, and $U(r)$ the interaction potential between them. If $\mathbf{T}(\mathbf{r})$ is set equal to zero, then one has the usual Smoluchowski form of the diffusion operator. The effect of $\mathbf{T}(\mathbf{r})$ in Eq. (1) is to lead to diffusion with an apparent space-dependent diffusion coefficient.

The added correction to the diffusion equation, given by Oseen's tensor, is clearly an approximation. Oseen's tensor is a good approximation when the sizes and separation of the radical pair are significantly larger than the size of the solvent molecules. However, this correction is in the same spirit as any Brownian diffusion treatment of molecular diffusion and diffusion controlled molecular reaction kinetics. One may hope to get useful insights about the general trends. In particular, the features of a space-dependent diffusion coefficient do not appear in any previous model considered, and as we shall see, that is the essential new feature of employing Oseen's tensor.

The method is based on numerical solutions of the stochastic Liouville equation:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = [-i\mathcal{K}(\mathbf{r})^x + \Gamma_{\mathbf{r}}] \rho(\mathbf{r}, t) \quad (1.3)$$

where $\mathcal{K}(\mathbf{r})$ is the spin Hamiltonian for the radical pair, and it is a function of the interrational separation via the exchange interaction $J(\mathbf{r})$.

Deutch points out that it was not possible to find an exact solution to the problem, although the finite difference method of Pedersen and Freed would be directly

applicable. This is indeed the case, and we report on the results of such a solution. Since the methods are identical to those discussed earlier,²⁻⁵ we do not discuss them further here other than to give the appropriate finite difference form [of Eq. (1.1a)] in an appendix. Our results are for radicals of equal radii which should exhibit the largest hydrodynamic effect.⁶ Then Eq. (1) becomes for spherical symmetry (so that $r-r$ is the only relevant variable):

$$\Gamma_r = r^{-2} \frac{\partial}{\partial r} (r^2) \left(D - \frac{kT}{2\pi\eta r} \right) \left[\frac{\partial}{\partial r} + (kT)^{-1} \frac{\partial U(r)}{\partial r} \right], \quad (1.1a)$$

where we have assumed equal sized radicals.

By introducing the transformation $\rho(r) \rightarrow r\rho(r) \equiv \hat{\rho}(r)$ and $\Gamma_r \rightarrow r\Gamma_r r^{-1} \equiv \hat{\Gamma}_r$, one finds that $\Gamma_r \rho(r) = r^{-1} \hat{\Gamma}_r \hat{\rho}(r)$. This yields an effective diffusion operator when $U=0$ for Oseen's tensor of $D(r)(\partial^2/\partial r^2)$, where $D(r) = D(1 - 3d/4r)$; but without Oseen's tensor (i.e., normal diffusion) this term is simply $D(\partial^2/\partial r^2)$. Similar changes are obtained for the other terms in Γ_r when $U(r) \neq 0$, and this justifies our remarks that the use of Oseen's tensor corresponds to an example of an apparent space dependent diffusion constant, which acts to retard the relative diffusion as the radicals approach.

II. RESULTS

A. CIDNP

We have already shown that the CIDNP phenomenon is very generally described in terms of two fundamental parameters⁵

$$\Lambda \equiv \mathcal{F}_0(S) \quad (2.1)$$

and

$$\mathcal{F}^* = \lim_{\Lambda \rightarrow 1} \mathcal{F}(T_0), \quad (2.2)$$

where \mathcal{F} is the probability the radicals in specific nuclear spin states react per collision. A "collision" includes the first encounter, as well as *all* possible re-encounters before the radicals finally diffuse away. Also \mathcal{F}_0 is the value of \mathcal{F} calculated for $Q=0$ where Q is half the difference in resonant frequencies of the radicals, i.e., \mathcal{F}_0 excludes any effects from singlet-triplet ($S-T_0$) mixing. The arguments S and T_0 in parenthesis refer to initially singlet or triplet spins. Thus Λ is *precisely* the fractional probability of reaction (for $Q=0$) of singlets for the whole "collision," and \mathcal{F}^* measures the conversion from triplets to singlets for the whole "collision."

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

Furthermore we can again write

$$\Lambda = k\tau_1 / (1 + k\tau_1), \quad (2.3)$$

where $k(r)$ is the rate of reaction of singlets when the radicals are in contact, and τ_1 is a characteristic lifetime of the interacting pair for the whole "collision."

In all the cases we have examined, we find that τ_1 may be exactly represented by

$$\tau_1^{-1} = \frac{D}{d\Delta r_k} \tilde{f}^* \exp\left[\frac{U(d)}{kT}\right], \quad (2.4)$$

where d is the contact distance of the two radicals, and the range of influence of $k(r)$ is d to $d + \Delta r_k$, and $\Delta r_k \ll d$. Also \tilde{f}^* obeys

$$(\tilde{f}^*)^{-1} = d \int_d^\infty \exp\left(\frac{U(r)}{kT}\right) \left[r \left(r - \frac{3d}{4} \right) \right]^{-1} dr. \quad (2.5)$$

This \tilde{f}^* replaces the quantity f^* given by

$$(f^*)^{-1} = d \int_d^\infty \exp\left(\frac{U(r)}{kT}\right) r^{-2} dr, \quad (2.6)$$

which was found to be appropriate in the absence of Oseen's tensor,⁵ and is the Debye-type correction found in the usual analyses of chemical-reaction kinetics. Typical results showing the Oseen's tensor correction to τ_1 are given in Table I. They show that Oseen's tensor effects increase τ_1 by the order of factors of 2, the effects being more pronounced in the presence of repulsive forces and less pronounced for attractive forces. This increase is expected for a mechanism that effectively slows the diffusion as the radicals approach each other.

Deutch has indicated that Oseen's tensor may be replaced by Stokes' tensor in the analysis.¹ This form is perhaps more accurate for considering short range hydrodynamic interactions.⁶ Note, however, that Eq. (2.5) follows from Eq. (2.6) by replacing r^2 by $r^2(1 - 3d/4r)$ which is equivalent to the transformation of $D \rightarrow D(r)$ [cf. the discussion after Eq. (1.1a)]. Therefore, one might expect that the use of Stokes' tensor,⁶ where

$$D(r) = r^2 \left[1 - \frac{3d}{4r} \left(1 - \frac{d^2}{12r^2} \right) \right] D$$

for equal size spherical molecules, would result in replacing r^2 in Eq. (2.6) by

TABLE I. Effects of Oseen's tensor on τ_1 , t_f , and \tilde{f}^* .

	κd^a	τ_1/τ_{1OS}^b	$t_f/t_{fOS}^{b,c}$	\tilde{f}^*/f^{*d}
Attraction	1/4	0.777	0.783	0.781
	1/2	0.739	0.745	0.744
	1	0.687	0.691	0.690
	2	0.633	0.635	0.633
No force		0.541	0.543	0.541
Repulsion	2	0.431	0.439	0.434
	1	0.392	0.399	0.393
	1/2	0.372	0.378	0.372
	1/4	0.364	0.371	0.364

^a κ is the Debye-Hückel reciprocal thickness of the ionic layer. Also a value of $|U(d)| = 5k_B T / (1 + \kappa d)$ was used.

^bThis is the ratio of τ_1 (or t_f) with Oseen's tensor neglected to the result including Oseen's tensor.

^c $r_f \sim 2000 \text{ \AA}$.

^dThis is the ratio of \tilde{f}^* with Oseen's tensor included to that neglecting it.

$$r^2 \left[1 - \frac{3d}{4r} \left(1 - \frac{d^2}{12r^2} \right) \right]$$

Such a replacement suggests that there would be little effect in the use of Stokes' tensor instead of Oseen's tensor. (Such comments would apply to the results below as well.)

In this context, it should be noted that Deutch and Felderhof⁶ have found that the mean rate of bimolecular encounters [in our notation $2k_2(d)$]³ is given in the case of Oseen's tensor by

$$2k_2(d) = 4\pi D \bar{f}^* \quad (2.7)$$

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

$$K = 2k_2(d)/\tau_1^{-1} \quad (2.8)$$

and it is of course independent of the molecular dynamics. Oseen's tensor only causes the diffusion to be space-dependent. It does not change $U(r)$. Thus K must be independent of whether or not Oseen's tensor is included. The fact that \bar{f}^* should appear in Eq. (2.4) is easily obtained analytically in the standard manner⁸ from the steady-state flux expressions given by Deutch and Felderhof.⁶

Furthermore we have found that t_f (where $1 - t_f$ is the total probability that two particles initially separated by r_I will never encounter at $r = d$) is well represented by the expression:

$$t_f = \bar{f}^* d / r_I \quad (2.9)$$

where $r_I \gg d$, by analogy with our previous result involving f^* instead of \bar{f}^* .⁵ More generally, one expects from our previous results that

$$t_f = 1 - \bar{f}^* / \bar{f}^*(r_I) \quad (2.10)$$

where

$$\bar{f}^*(r_I)^{-1} = d \int_d^{r_I} \exp\left[\frac{U(r)}{kT}\right] \frac{dr}{r(r-3/4d)} \quad (2.11)$$

such that

$$\bar{f}^* = \lim_{r_I \rightarrow \infty} \bar{f}^*(r_I)$$

As we have previously noted (see Ref. 12a in III) such results are expected to follow from a simple argument based upon an analysis of k_f , the experimentally observed rate constant for the reaction including diffusion for steady-state fluxes. Thus we may write^{4,5}

$$\begin{aligned} k_f &= \Lambda 2k_2(d) \\ &= \Lambda t_f(r_I) 2k_2(r_I) \end{aligned} \quad (2.12)$$

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

$$t_f(r_I) = k_2(d)/k_2(r_I) \quad (2.13)$$

which is seen to yield Eq. (2.10) by using Eq. (2.7) and the equivalent expression for $k_2(r_I)$. Typical results of the effects of Oseen's tensor on t_f are shown in Table I.

We now turn to an analysis of \mathcal{F}^* . Again Eq. (3.11) of III which relate $\mathcal{F}(T_0)$, $\mathcal{F}(S)$, and $\mathcal{F}(R.I.)$ to \mathcal{F}^* and Λ are found to apply exactly. We give in Figs. 1(a) and (b) the corrections to \mathcal{F}^* due to Oseen's tensor for attractive and repulsive (shielded) Coulomb forces and no forces. As was the case for τ_1 , repulsive forces yield greater effects than no forces and attractive forces yield smaller effects. In general, the greater effects are obtained for small values of Qd^2/D . In fact, the ratios $\mathcal{F}_{OS}^*/\mathcal{F}_N^*$ (cf. Fig. 1) appear to be approaching those of $\tau_1/\tau_1(OS)$ (cf. Table I) as $Qd^2/D \rightarrow 0$. But for large values of Qd^2/D , the ratios $\mathcal{F}_{OS}^*/\mathcal{F}_N^*$ appear to approach unity, an effect most pronounced for attractive forces. The result for small values is easily interpreted by recognizing in this region, in the absence of potentials and Oseen's tensor effects (for small J_0):

$$\mathcal{F}^* = \frac{1}{2} \sqrt{Qd^2/D} \quad (2.14)$$

and one should to a first approximation replace d by f^*d (or \bar{f}^*d), i.e., this is the region where re-encounters after large separations are important, so the dominant effect of the shorter range interactions is to introduce an effective contact distance into the dynamics. For larger Qd^2/D , Eq. (2.14) is no longer appropriate,⁵

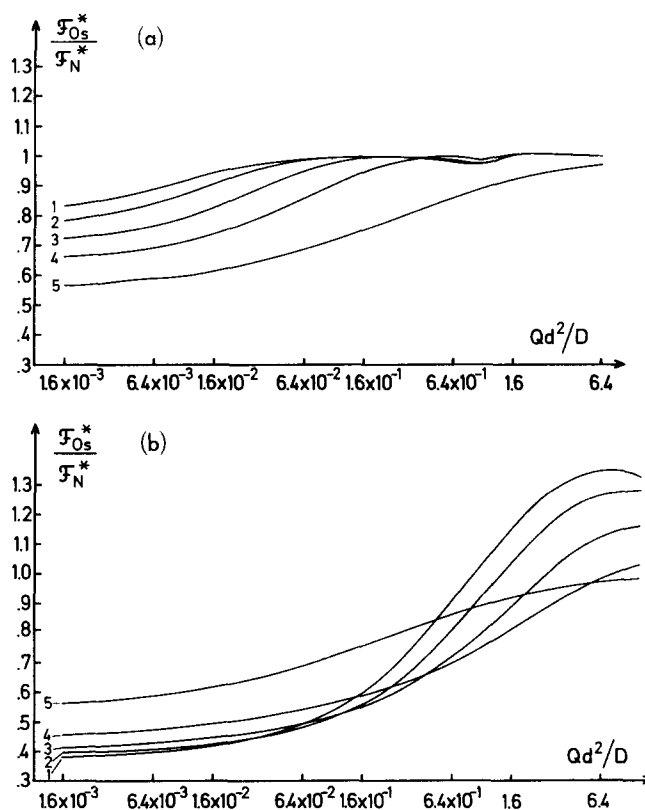


FIG. 1. Graphs of $\mathcal{F}_{OS}^*/\mathcal{F}_N^*$ vs the dimensionless variable Qd^2/D . Here \mathcal{F}_{OS}^* is the value for \mathcal{F}^* calculated with Oseen's tensor and \mathcal{F}_N^* is the value neglecting Oseen's tensor. Curves 1, 2, 3, 4, and 5 are, respectively for $\kappa d = \frac{1}{4}, \frac{1}{2}, 1, 2$, and no Coulomb forces (where κ is the usual Debye-Hückel reciprocal thickness of the ionic layer and $|U(d)| = 5k_B T / (1 + \kappa d)$). Figure 1(a) shows results for attractive shielded Coulombic forces, while Fig. 1(b) gives results for repulsive shielded Coulombic forces. A low value of $J_0 = 10^5 \text{ sec}^{-1}$ has been used (cf. III).

the effects of the initial encounter become more important and one has $\mathfrak{F}^* \propto (Qd^2/D)^\epsilon$ with $\epsilon < \frac{1}{2}$, so the dependence of \mathfrak{F}^* decreases. One should note that Fig. 1 is calculated for a very small value of the exchange interaction $J_0 = 10^6 \text{ sec}^{-1}$, which serves to exclude any effect of a finite exchange region. Some of our numerical results for more realistic values of J_0 are given in Table II. In general the effect of larger J_0 values (that increases with increasing J_0 and r_{EX}/d) is to decrease $\mathfrak{F}_{\text{OS}}^*/\mathfrak{F}_N^*$. For $Q = 10^8 \text{ sec}^{-1}$, $d = r_{\text{EX}} = 4 \text{ \AA}$, and $D = 10^{-4} \text{ cm}^2/\text{sec}$, this reduction is negligible but for $D = 10^{-6} \text{ cm}^2/\text{sec}$ there is a reduction of approximately 20%. These dependences may be understood by arguments similar to those used in III. The trajectories in the exchange region become more important when J_0 (and r_{EX}/d) increases and D decreases (i.e., the diffusion slows down). In the exchange region the Q mixing is suppressed and consequently \mathfrak{F}^* is decreased. Since the Oseen's correction to the diffusion equation corresponds to a slow down of the diffusion when the particles are close together one would expect $\mathfrak{F}_{\text{OS}}^*$ to decrease more than \mathfrak{F}_N^* as is indeed observed from the numerical results.

B. CIDEP

In the theory of CIDEP, we have found P_a^∞ , the asymptotic polarization of radical a as the radical pair separates, to be the important new quantity.^{3,4} Furthermore, one may readily relate the polarizations generated in the presence of a spin-selective chemical reaction to those in its absence by

$$P^\infty(\text{R. I.})/\mathfrak{F}(\text{R. I.}) = -P_{k=0}^\infty(S) = P_{k=0}^\infty(T), \quad (2.15)$$

where the subscript $k=0$ indicates no chemical reaction.^{3,4} The quantity $\mathfrak{F}(\text{R. I.})$ is often approximated as $\mathfrak{F}_0(\text{R. I.}) = \frac{1}{2} \Lambda$ and the small corrections may be obtained from Eqs. (3.3)–(3.5) of Ref. 5 and the discussions in Sec. II. A on \mathfrak{F} .

Our results on P^∞/\mathfrak{F} for R. I. are given in Fig. 2. They include shielded Coulomb interactions as well as no charge interactions. We give results in the two limiting cases of low J_0 and high J_0 . In order to interpret these results we briefly review the results neglecting Oseen's tensor.²⁻⁴ For no interactions they were found to be approximated for a $J(r)$ given by

$$J(r) = J_0 e^{-(r-d)\lambda} \quad r \geq d$$

by

$$P_a^\infty \approx \left(\frac{Qd^2}{D}\right)^\epsilon 2J_0\tau_1(\lambda), \quad \text{for } 2J_0\tau_1(\lambda) \ll 1 \quad (2.16)$$

with

$$\tau_1(\lambda) \approx (d/D\lambda) [1 + (\lambda d)^{-1}] \quad (2.17)$$

and by

$$P_a^\infty \approx (Qd^2/D)^\epsilon \sqrt{2}/(\lambda d)^{\epsilon'}, \quad \text{for } 2J_0\tau_1(\lambda) \gg 1, \quad (2.18)$$

independent of J_0 . In these expressions, $\epsilon \sim \frac{1}{2}$ for $(Qd^2/D) \leq 0.016$ but $\epsilon \rightarrow 0$ as Qd^2/D becomes larger. Also $\epsilon' \sim 1$ for $\lambda d \gg 1$ and $(Qd^2/D) < 0.016$ but becomes smaller as these inequalities are violated. These formulas can be incorporated in the form

$$P_a^\infty \approx \left(\frac{Qd^2}{D}\right)^\epsilon \frac{2J_0\tau_1(\lambda) + [1.5/(\lambda d)^{\epsilon'}] [2J_0\tau_1(\lambda)]^2}{1 + [2J_0\tau_1(\lambda)]^2}, \quad (2.19)$$

which approximates the over-all behavior, but is not exact.

The general effects of attractive and repulsive forces on P^∞/\mathfrak{F} were found in II to be complex with typically opposite trends depending upon whether J_0 was large or small. The general trend for small J_0 is in accord with the trend (but not the quantitative values) obtained by (1) letting $\tau(\lambda)$ in Eq. (2.16) have the dependence upon $f^* e^{U(d)/kT}$ of Eq. (2.4) and (2) letting $(Qd^2/D)^\epsilon$ in Eq. (2.16) have the charge dependence characteristic of \mathfrak{F}^* as discussed in III and the previous section. [Note,

TABLE II. Effect of Oseen's tensor on P^∞/\mathfrak{F} and \mathfrak{F}^* .^{a,b}

$J_0 \text{ sec}^{-1}$	$D = 10^{-4} \text{ cm}^2/\text{sec}$			$D = 10^{-6} \text{ cm}^2/\text{sec}$		
	At. $\kappa d = 0.25^c$	No force	Rep. $\kappa d = 0.25^c$	At. $\kappa d = 0.25^c$	No force	Rep. $\kappa d = 0.25^c$
10^5	1.21 (0.83)	1.20 (0.56)	1.35 (0.39)	1.28 (0.98)	1.84 (0.75)	2.74 (0.60)
10^7	1.21 (0.83)	1.20 (0.56)	1.34 (0.39)	1.28 (0.98)	1.84 (0.75)	2.74 (0.60)
10^9	1.21 (0.83)	1.20 (0.56)	1.34 (0.39)	0.88 (0.94)	1.66 (0.73)	2.71 (0.60)
10^{11}	0.75 (0.82)	1.05 (0.56)	1.33 (0.39)	2.07 (0.94)	1.53 (0.67)	1.38 (0.51)
10^{13}	2.05 (0.82)	1.20 (0.57)	0.88 (0.39)	1.49 (0.90)	1.32 (0.63)	1.24 (0.47)
10^{15}	1.43 (0.82)	1.12 (0.56)	0.93 (0.39)	1.32 (0.87)	1.25 (0.61)	1.20 (0.45)

^aThe values given are $[P^\infty/\mathfrak{F}]_{\text{OS}}/[P^\infty/\mathfrak{F}]$ and $\mathfrak{F}_{\text{OS}}^*/\mathfrak{F}$ (in parenthesis).

^bOther parameters used are $Q = 10^8 \text{ sec}^{-1}$, $r_{\text{EX}} = d = 4 \text{ \AA}$, $\Delta r = 0.25 \text{ \AA}$, $M = 200$, $N = 400$, $r_N = 5054 \text{ \AA}$, and $|U(d)| = 5k_B T/(1 + \kappa d)$.

^cAt. and Rep. stands for attractive and repulsive shielded Coulomb forces, respectively.

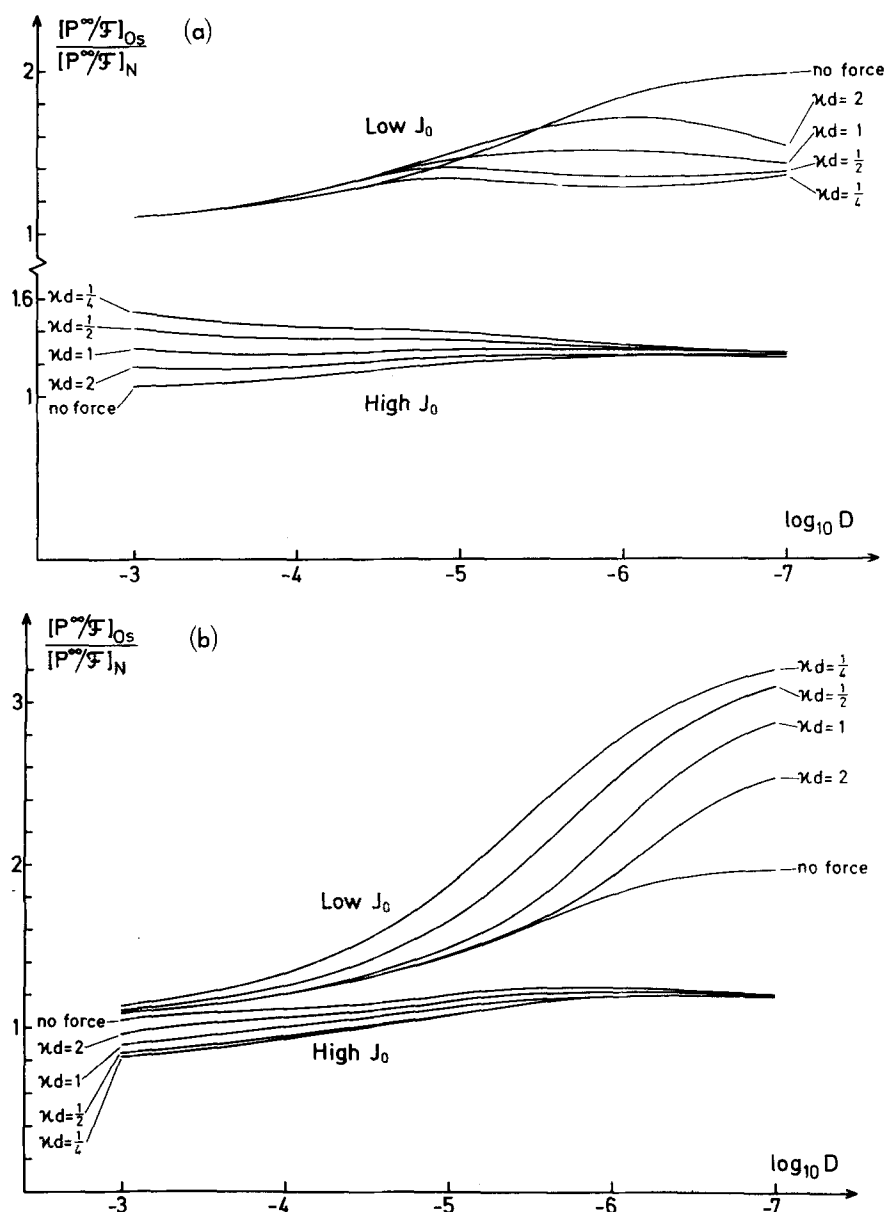


FIG. 2. Graphs of $[P^{\infty}/\mathfrak{F}]_{OS}/[P^{\infty}/\mathfrak{F}]_N$ vs D . Here the subscripts OS and N refer to results calculated with Oseen's tensor and neglecting Oseen's tensor, respectively. Figure 2(a) shows results for attractive shielded Coulombic forces, while Fig. 2(b) gives results for repulsive shielded Coulombic forces. The low J_0 results (upper curves) were calculated with $J_0 = 10^5 \text{ sec}^{-1}$, while the high J_0 results (lower curves) are for $J_0 = 10^{15} \text{ sec}^{-1}$. Note that κ is the usual Debye-Hückel reciprocal thickness of the ionic layer and $|U(d)| = 5k_B T / (1 + \kappa d)$. Other parameters used are $Q = 10^8 \text{ sec}^{-1}$, $r_{EX} = 5 \ln 10 / \lambda = d = 4 \text{ \AA}$.

however, that the Q dependence of the polarization is not the same for CIDEP as that for CIDNP. This reflects the different consecutive steps needed to create the respective polarizations (cf. III). In particular, for CIDEP ϵ will change from its limiting value of $\frac{1}{2}$ (for $Qd^2/D \ll 1$) much sooner (i. e., for much smaller values of Qd^2/D) than is the case for CIDNP. This fact limits the quantitative validity of the arguments given for the trends]. For large J_0 the asymptotic polarizations, which develop in spatial regions where $r > d$, are much less sensitive to charge effects.

Our present results with Oseen's tensor may be rationalized in terms of similar trends. That is for small J_0 , $[P^{\infty}/\mathfrak{F}]_{OS}/[P^{\infty}/\mathfrak{F}]_N$ shows trends predicted by the product of τ_{1OS}/τ_1 and $\mathfrak{F}_{OS}^*/\mathfrak{F}^*$ as expected from Eq. (2.16). For $Qd^2/D < 0.016$ we have $\epsilon = \frac{1}{2}$ in Eq. (2.16), i. e., $\mathfrak{F}^* = (Qd^2 \bar{f}^{*2}/D)^{1/2}$ and consequently $[P^{\infty}/\mathfrak{F}]_{OS}/[P^{\infty}/\mathfrak{F}]_N = 1$. For larger Qd^2/D values $\epsilon \rightarrow 0$ and we get $[P^{\infty}/\mathfrak{F}]_{OS}/[P^{\infty}/\mathfrak{F}]_N \rightarrow f^*/\bar{f}^*$. These effects are such as to increase P^{∞}/\mathfrak{F} by a factor of the order 1.1–3. The results for

high J_0 typically show only a small effect from Oseen's tensor, since the region of $r \sim d$, for which Oseen's tensor corrections are a maximum, have become relatively unimportant in the polarization process. A more quantitative discussion of the behavior for large J_0 does not seem possible at present because we only have a very qualitative understanding of Eq. (2.18) even in the absence of forces. For intermediate values of J_0 the qualitative behavior is given by Eq. (2.19). One should note that J_{max} , the value of J_0 that gives maximum polarization (cf. I), is given by $2J_{max}\tau_1(\lambda) \approx 1$, and, since τ_{1OS} and τ_1 are different, the maximum occurs for different values of J_0 and consequently $[P^{\infty}/\mathfrak{F}]_{OS}/[P^{\infty}/\mathfrak{F}]_N$ can show an oscillation for intermediate J_0 values. A few of our results for intermediate J_0 values are given in Table II.

III. CONCLUSIONS

Detailed results for Oseen's tensor effects upon CIDNP and CIDEP have been obtained by means of the finite-difference solution to the stochastic-Liouville

equation. For this prototype model of a space-dependent diffusion coefficient an exact expression was found for τ_1 , the effective lifetime of the reacting radical pair. This expression may be indicative of a general form for other space-dependent diffusion coefficients. One finds that τ_1 is increased by factors of 2, with somewhat larger effects in the presence of repulsive forces, but smaller effects for attractive effects. The closely related quantity, the re-encounter probability showed nearly the same effects.

The fundamental quantity for CIDNP (\mathcal{F}^*) is approximately affected inversely as the τ_1 correction for the range $Qd^2/D < 10^{-1}$ which corresponds to most cases of normal liquids, and this correction is fairly constant over this range. Thus the relative dependences of the polarization upon Q , the hyperfine difference, an important experimental quantity, is not significantly affected. For very viscous liquids for which $Qd^2/D \geq 1$, the Oseen tensor corrections become negligible.

The effect of Oseen's tensor on the CIDEP quantity P_a^∞/\mathcal{F} is generally quite small for large values of J_0 (usually $J_0 \geq 10^{12} \text{ sec}^{-1}$ but more precisely $J_0 d/D\lambda > 1$) and may in most cases be neglected. For small values of J_0 (usually $\leq 10^{10} \text{ sec}^{-1}$ but more precisely $J_0 d/D\lambda < 1$) substantial effects are encountered only in more viscous media with $D < 10^{-5} \text{ cm}^2/\text{sec}$. Again, except for this last case of small J_0 and D , the relative dependence upon Q for different hyperfine states is essentially unaffected.

These prototype results then indicate that for space-dependent diffusion coefficients, which include a retardation of the relative diffusion as radicals approach, the retardation will in most cases tend to reflect itself in a nearly constant correction (of order 1-2) to the polarization for reasonable experimental variation in relevant parameters, D and Q .

APPENDIX

W matrix^{3,4}

$$yW_{0,0} = 2 + \frac{2\Delta r}{d} - \frac{6}{4} \left(1 + \frac{\Delta r}{2d}\right) - \frac{2r_1}{d} \left[1 - \frac{3}{4} \frac{d}{r_1}\right] \tilde{F}(1),$$

$$yW_{0,1} = -2 + \frac{6}{4} \left(1 - \frac{\Delta r}{2d}\right) - 2\tilde{F}(0) \left[1 - \frac{3}{4}\right].$$

For $0 < i < M$ use

$$yW_{i,i-1} = -1 + \frac{3d}{4r_i} \left[1 + \frac{\Delta r}{2r_{i-1}}\right] + \tilde{F}(i) \left[1 - \frac{3d}{4r_i}\right],$$

$$yW_{i,i} = 2 - \frac{6d}{4r_i} - \tilde{F}(i+1) \left[\frac{r_{i+1}}{r_i} - \frac{3d}{4r_i}\right] + \tilde{F}(i-1) \left[\frac{r_{i-1}}{r_i} - \frac{3d}{4r_i}\right],$$

$$yW_{i,i+1} = -1 + \frac{3d}{4r_i} \left[1 - \frac{\Delta r}{2r_{i+1}}\right] - \tilde{F}(i) \left[1 - \frac{3d}{4r_i}\right].$$

Then

$$yW_{M,M-1} = \frac{2}{(1+f)} \left[-1 + \frac{3d}{4r_M} \left(1 + \frac{\Delta r}{2r_{M-1}}\right) + \tilde{F}(M) \left(1 - \frac{3d}{4r_M}\right)\right],$$

$$yW_{M,M} = \frac{2}{f} - \frac{1}{f} \frac{6d}{4r_M} - \frac{\tilde{F}(M+1)2}{f(1+f)} \left(\frac{r_{M+1}}{r_M} - \frac{3d}{4r_M}\right) + \frac{\tilde{F}(M-1)2}{(1+f)} \left(\frac{r_{M-1}}{r_M} - \frac{3d}{4r_M}\right),$$

$$yW_{M,M+1} = \frac{2}{f(1+f)} \left[-1 + \frac{3d}{4r_M} \left(1 - \frac{\Delta r f}{2r_{M+1}}\right) - \tilde{F}(M) \left(1 - \frac{3d}{4r_M}\right)\right].$$

For $M < i < N$ use this expression for $0 < i < M$ with the appropriate value of r , but change Δr to $\Delta r f$ and then multiply the total expression by f^{-2} .

Also $W_{N-1,N} = 0$,

$$W_{N,N-1} = f^{-2} \left[-2 + \frac{6d}{4r_N} \left(1 + \frac{\Delta r f}{2r_{N-1}}\right) + 2\tilde{F}(N) \left(1 - \frac{3d}{4r_N}\right)\right],$$

$W_{N,N} = 0$.

Also $y = -\Delta r^2/D$ and $\tilde{F}(i) \equiv \frac{1}{2} \Delta r F(i)$.

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