

CHAPTER XIX

NUMERICAL METHODS AND MODEL DEPENDENCE IN CHEMICALLY-INDUCED DYNAMIC SPIN POLARIZATION*

Jack H. Freed

Department of Chemistry, Cornell University,
Ithaca, New York 14853

In this chapter we describe some of the more advanced theoretical methods, which may be usefully employed in the study of chemically-induced spin polarization and related phenomena. The emphasis will be on the finite difference methods developed by Pedersen and Freed [1-6].

1. SOLUTIONS OF THE DIFFUSION EQUATION

1.1 The diffusion equation

Let us consider the diffusion equation:

$$\frac{\partial p(\vec{r}, t)}{\partial t} = D \Gamma_{\vec{r}} p(\vec{r}, t) \quad (1.1)$$

where $p(\vec{r}, t)$ is the classical probability or distribution function for motion of a particle (or, in the present problem, the relative motion of a pair of particles), while $D \Gamma_{\vec{r}} = D \nabla_{\vec{r}}^2$ is the Markovian operator for the diffusion with diffusion coefficient D . When the problem admits of spherical symmetry (i.e., any potential terms in $D \Gamma_{\vec{r}}$ depend only on $r = |\vec{r}|$ and any boundary conditions depend only on r), then it is most convenient to write $\Gamma_{\vec{r}}$ in spherical polar coordinates in the form:

$$\Gamma_{\vec{r}} = \Gamma_r + (1/r^2) \Gamma_{\Omega} \quad (1.2a)$$

* This work has been supported in part by a grant (CHE 75-00938) from the National Science Foundation.

where, for Brownian motion in the absence of potentials, Γ_r , the radial part is given by

$$\Gamma_r = (1/r^2)(\partial/\partial r)r^2(\partial/\partial r) \quad (1.2b)$$

while the angular part Γ_Ω , is:

$$\Gamma_\Omega = (1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)] + (1/\sin^2\theta)(\partial^2/\partial\theta^2) \quad (1.3)$$

We then can focus on the radial part of the distribution function:

$$p(r,t) = (1/4\pi) \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi p(\vec{r},t) \quad (1.4)$$

which obeys the diffusion equation:

$$\partial p(r,t)/\partial t = D\Gamma_r p(r,t) \quad (1.5)$$

1.2 Eigenfunction solutions

The solution to this diffusion equation is well known, and may be expressed as a conditional probability function, or Green's function:

$$\begin{aligned} p(\vec{R};\vec{r},t) &= (4\pi Dt)^{-3/2} \exp\left\{-\frac{(\vec{r}-\vec{R})^2}{4Dt}\right\} \\ &= \frac{1}{(2\pi)^3} \int \exp\{-i(\vec{r}-\vec{R})\cdot\vec{\rho} - \rho^2 Dt\} d^3\rho \end{aligned} \quad (1.6)$$

Then by using the usual spherical Bessel function expansion of $e^{i\vec{\rho}\cdot\vec{r}}$ as well as the addition formula for the Legendre polynomials and their orthonormal properties, one has

$$p(|\vec{r}-\vec{R}|,t) = \frac{1}{2\pi^2} \int_0^\infty e^{-\rho^2 Dt} j_0(\rho R) j_0(\rho r) \rho^2 d\rho \quad (1.7)$$

where $j_0(\rho r)$ is the zero order spherical Bessel function; $j_0(z) \equiv \sin z/z$. This result may be understood as an expansion of the solution in the Hilbert space spanned by the $j_0(\rho r)$ for each different value of r . That is, we may regard this as an expansion in the orthonormal eigenkets:

$$|G_{\ell m}(\vec{\rho},\vec{r})\rangle \equiv \left|\sqrt{\frac{2}{\pi}} j_\ell(\rho r) Y_\ell^m(\Omega)\right\rangle \quad (1.7a)$$

where, because of spherical symmetry, we will only be interested in the $\ell = m = 0$ terms. Thus, we have:

$$p(\vec{R}; \vec{r}, t) = \int_0^\infty \rho^2 d\rho \sum_{\ell m} |G_{\ell m}(\vec{\rho}, \vec{r})\rangle e^{-\rho^2 D t} \langle G_{\ell m}(\vec{\rho}, \vec{R})| \quad (1.8)$$

and $p|\vec{r}-\vec{R}\rangle, t)$ is obtained from this equation by setting $\ell = m = 0$, to yield the result of eq. 1.7.

Let us now note some useful variations on this formula. If the space is bounded by some outer wall (e.g., the walls of the container) taken to be spherical, then the integral over ρ becomes a sum over ρ corresponding to those discrete values of ρ which satisfy this outer boundary [7]. Of more use is the case of an inner boundary at $r = d$ corresponding to closest contact; thus we have as the range of r : $d \leq r < \infty$. In this case, one replaces the $|G_{\ell m}(\vec{\rho}, \vec{r})\rangle$ by the correct eigenfunctions given by Carslaw and Jaeger [7] which include appropriate linear combinations of Bessel functions. Let us call them $|\hat{G}_{\ell m}(\vec{\rho}, \vec{r})\rangle$. Now the inner boundary condition will be purely reflective if there is no reaction, but will be at least partially absorptive if there is a finite reactivity. Collins and Kimball [8] considered such a boundary for chemical kinetics. It may be written as:

$$\bar{k}_p(d) = D(\partial p / \partial r)_{r=d} \quad (1.9)$$

and it states that the probability flux into $r < d$ [given by $D(\partial p / \partial r)_d$] is equal to the rate of reaction at the surface [given by $\bar{k}_p(d)$] where \bar{k} plays the role of a reactivity. [In Carslaw and Jaeger's [7] notation $h \equiv \bar{k}/D$.] (We will relate it to a first order rate constant below.) From Collins and Kimball's treatment, one has that the steady-state rate constant, which may be experimentally observed, is

$$k_f = \Lambda 2k_2(d) \quad (1.10)$$

where $2k_2(d) = 4\pi dD$ is the rate of new bimolecular encounters, and we have [6] that Λ is then the fractional probability of reaction. The CK result is:

$$\Lambda = \frac{d\bar{k}/D}{1 + d\bar{k}/D} \quad (1.11)$$

so for $\Lambda \ll 1$, one has $k_f = 4\pi d^2 \bar{k}$, and it is independent of the diffusion, as it should be. (Below, we compare this result with that from finite differences). One has obtained an analytical solution to this problem (cf. [8]). [Another approach is to use the boundary condition of eq. 1.9 but with $h = \bar{k} = 0$, i.e., a pure reflecting wall. Then it is necessary to introduce a reaction at $r = d + \epsilon$. This is utilized in the finite difference method below].

Now suppose we must generalize the diffusion equation to include, for example, some potential of interaction. That is, we would have a Smoluchowski equation for the relative diffusion:

$$\frac{d\vec{p}(\vec{r}, t)}{dt} = D\nabla_{\vec{r}}^2 \vec{p} + (D/kT)\vec{\nabla}_{\vec{r}} \cdot [\vec{p}(\vec{\nabla}_{\vec{r}} U(r))] \equiv D\vec{\Gamma}_{\vec{r}} \vec{p} \quad (1.12)$$

where $U(r)$ is the potential energy between particles assumed to depend only on r . The new $\vec{p}(\vec{r}, t)$ will no longer be expressible in terms of the $|\mathcal{G}_{\ell m}(\vec{\rho}, \vec{r})\rangle$ or $|\hat{\mathcal{G}}_{\ell m}(\vec{\rho}, \vec{r})\rangle$. Instead, our solution will be expressible in new eigenkets, each of which may be written as an expansion in the $|\hat{\mathcal{G}}_{\ell m}(\vec{\rho}, \vec{r})\rangle$. The expansion coefficients may then be obtained by perturbation theory, when applicable, or by some other methods. Actually, it is easier to work with a symmetrized form of eq. 1.12. That is, let $p_0(\vec{r})$ be a measure of the equilibrium probability distribution such that $p_0(\vec{r}_1)/p_0(\vec{r}_j)$ is the ratio of probability of finding the radical-pair separated by \vec{r}_1 to that for \vec{r}_j (e.g., let $p_0(\vec{r}) = e^{-U(r)/kT}$). Then let

$$\tilde{p}(\vec{r}, t) \equiv [p_0(\vec{r})]^{-1/2} p(\vec{r}, t) \quad (1.13)$$

and

$$\tilde{\Gamma}_{\vec{r}} \equiv [p_0(\vec{r})]^{-1/2} \vec{\Gamma}_{\vec{r}} [p_0(\vec{r})]^{1/2}$$

Then, one can show that eq. 1.12 becomes:

$$\frac{d\tilde{p}(\vec{r}, t)}{dt} = D\tilde{\Gamma}_{\vec{r}} \tilde{p} = D\nabla_{\vec{r}}^2 \tilde{p} + \frac{D\tilde{p}(\vec{\nabla}_{\vec{r}}^2 U(r))}{2kT} + \frac{D|\vec{F}(\vec{r})|^2}{(2kT)^2} \tilde{p} \quad (1.14)$$

where

$$\vec{F}(\vec{r}) \equiv -\vec{\nabla}_{\vec{r}} U(r)$$

which results in $\tilde{\Gamma}_{\vec{r}}$ being a Hermitian operator. One may then, for example, introduce perturbation theory to handle $U(r) \neq 0$. Thus, let us first take the Laplace transform of eq. 1.14 to give

$$\vec{p}(\vec{r}, s) = [s - D\vec{\Gamma}_{\vec{r}}]^{-1} \vec{p}(\vec{r}, 0) \quad (1.15)$$

with

$$\vec{p}(\vec{r}, s) \equiv \int_0^{\infty} e^{-st} \tilde{p}(\vec{r}, t) dt \quad (1.15a)$$

Then with

$$\tilde{\Gamma}_{\vec{r}}^0 \equiv \nabla_{\vec{r}}^2$$

while

$$\tilde{\Gamma}_{\vec{r}}^1 \equiv (\vec{\nabla}_{\vec{r}}^2 U(r))/2kT + |\vec{F}(\vec{r})|^2/(2kT)^2 \quad (1.16)$$

as the perturbation, one may use a resolvent-type approach [9] to give:

$$[s - D\tilde{\Gamma}_{\vec{r}}]^{-1} = \sum_{n=0}^{\infty} \left[\frac{1}{s - D\tilde{\Gamma}_{\vec{r}}^0} (-D\tilde{\Gamma}_{\vec{r}}^1) \right]^n \frac{1}{s - D\tilde{\Gamma}_{\vec{r}}^0} \quad (1.17)$$

The conditional probability solution is obtained by letting

$$p(\vec{R}, \vec{r}, 0) = \delta(\vec{r} - \vec{R}) = \int_0^{\infty} \rho^2 d\rho \sum_{\ell, m} |\hat{G}_{\ell m}(\vec{\rho}, \vec{r})\rangle \langle \hat{G}_{\ell m}^*(\vec{\rho}, \vec{R})| \quad (1.18)$$

Note that the zero-order solution (i.e., $n = 0$) is just the Laplace transform of eq. 1.8, as it should be. However, the first order correction is given by

$$\begin{aligned} \bar{p}(\vec{R}, \vec{r}, s) \rangle^{(1)} &= \int_0^{\infty} \rho'^2 d\rho' \sum_{\ell', m'} |\hat{G}_{\ell' m'}(\rho', r')\rangle \times \\ &\int_0^{\infty} \rho^2 d\rho \sum_{\ell, m} \frac{\langle \hat{G}_{\ell' m'}(\vec{\rho}', \vec{r}') | -D\tilde{\Gamma}_{\vec{r}}^1 | \hat{G}_{\ell m}(\vec{\rho}, \vec{r}) \rangle}{s + D\rho'^2} \times \\ &\frac{1}{s + D\rho^2} \langle \hat{G}_{\ell m}^*(\vec{\rho}, \vec{R})| \end{aligned} \quad (1.19)$$

i.e., one must evaluate the matrix-elements (in \vec{r} space) of $\langle G_{\ell' m'}(\vec{\rho}', \vec{r}') | \tilde{\Gamma}_{\vec{r}}^{-1} | \hat{G}_{\ell m}(\vec{\rho}, \vec{r}) \rangle$. For a spherically symmetric $\tilde{\Gamma}_{\vec{r}}^{-1}$, we would get $\ell' = \ell$ and $m' = m$. In a similar manner, one can generate higher-order corrections. A variety of procedures for accomplishing this has been compared by Yoon, Deutch, and Freed [9]. A powerful technique that lends itself to numerical solutions, involves starting with eq. 1.15 and then expanding $\bar{p}(\vec{r}, s)$ (this is not the conditional probability) in a complete orthonormal set, e.g., the $\hat{G}_{\ell m}(\vec{\rho}, \vec{r})$:

$$|\bar{p}(\vec{r}, s)\rangle = \int \rho^2 d\rho \sum_{\ell, m} C_{\ell m}(\vec{\rho}, s) |\hat{G}_{\ell m}(\vec{\rho}, \vec{r})\rangle \quad (1.20)$$

Then by rewriting eq. 1.15 in the form

$$[s - D\tilde{\Gamma}_{\vec{r}}] |\bar{p}(\vec{r}, s)\rangle = |p(\vec{r}, 0)\rangle \quad (1.15')$$

and then pre-multiplying by $\langle \hat{G}_{\ell' m'}(\vec{\rho}', \vec{r}') |$ one obtains a set of coupled integral equations for the expansion coefficients $C_{\ell m}(\vec{\rho}, s)$:

$$\int \rho^2 d\rho \sum_{\ell, m} \langle \hat{G}_{\ell, m}(\vec{\rho}', \vec{r}) | (s - D\vec{\Gamma}_{\vec{r}}) | \hat{G}_{\ell m}(\vec{\rho}, \vec{r}) \rangle C_{\ell m}(\vec{\rho}, s) = \langle \hat{G}_{\ell, m}(\vec{\rho}', \vec{r}) | p(\vec{r}, 0) \rangle \quad (1.21)$$

Note that the coefficient of $C_{\ell m}(\vec{\rho}, s)$ in eq. 1.21 may be rewritten as:

$$\int \rho^2 d\rho \sum_{\ell, m} [(s + \rho^2 D) \delta_{\ell\ell'} \delta_{mm'} \delta(\vec{\rho} - \vec{\rho}')] + \langle \hat{G}_{\ell, m}(\vec{\rho}', \vec{r}) | \vec{\Gamma}_{\vec{r}}(1) | \hat{G}_{\ell m}(\vec{\rho}, \vec{r}) \rangle \quad (1.22)$$

This then again involves calculating the same matrix elements as above.

Now what are the typical questions asked about $p(\vec{r}, t)$ [or $\bar{p}(\vec{r}, s)$]? In one case we might want to ask for the total probability over all space $d \leq r < \infty$. Suppose, for the moment, we have $U = 0$. Then this corresponds to just the coefficient $C_{0,0}(0, s)$. That is

$$\langle \bar{p}(\vec{r}, s) \rangle_{Av} \equiv \int_d d^3\vec{r} \bar{p}(\vec{r}, s) = C_{0,0}(0, s) = \langle \hat{G}_{0,0}(0, \vec{r}) | \bar{p}(\vec{r}, s) \rangle \quad (1.23)$$

where the last two equalities follow from the use of eq. 1.20. This quantity will be unity, unless there is a reaction which depletes radicals (e.g., \bar{k} in eq. 1.9 is non-zero). Thus one must calculate in eq. 1.21 (or eq. 1.19) how the coefficient $C_{0,0}(0, s)$ couples to the other coefficients $C_{\ell, m}(\vec{\rho}, s)$ by the perturbation $\vec{\Gamma}_{\vec{r}}(1)$, which need not be small (but we are assuming it is spherically symmetric). When there is a non-uniform equilibrium distribution, i.e., $p_0(\vec{r}) \neq \text{constant}$, then the averaging prescription becomes:

$$\langle \bar{p}(\vec{r}, s) \rangle_{Av} \equiv \int_d d^3\vec{r} [p_0(\vec{r})]^{1/2} \bar{p}(\vec{r}, s) = \langle [p_0(\vec{r})]^{1/2} | \bar{p}(\vec{r}, s) \rangle \quad (1.24)$$

In the absence of a chemical reaction, $[p_0(\vec{r})]^{1/2}$ will correspond to the zero eigenvalue solution of $\vec{\Gamma}_{\vec{r}}$, i.e., it represents the conservation of probability over all space, which is unaffected by the diffusion.

Another question might be the probability of finding the particles separated by \vec{r}' at time t . One then needs

$$\langle \delta(\vec{r}-\vec{r}') | \bar{p}(\vec{r},s) \rangle = \int_0^\infty \rho^2 d\rho \sum_{\ell,m} \hat{G}_{\ell m}^*(\vec{\rho},\vec{r}') C_{\ell m}(\vec{\rho},s) \quad (1.25)$$

which follows from the form of the Dirac-delta function (eq. 1.18), and it involves a knowledge of all the $C_{\ell m}(\vec{\rho},s)$. Alternatively, we may just ask for a particular radial separation and use $\delta(|r|-|r'|)$. Then, it follows from eq. 1.7, that eq. 1.25 would become:

$$\langle \delta(|r|-|r'|) | \bar{p}(\vec{r},s) \rangle = \int_0^\infty \rho^2 d\rho \hat{G}_{00}^*(\vec{\rho},\vec{r}') C_{0,0}(\vec{\rho},s) \quad (1.26)$$

1.3 Numerical methods and eigenfunction solutions

An equation like eq. 1.21 may be solved numerically by replacing the integral over ρ by a sum. In fact, this will occur naturally if one introduces a finite outer wall at $r = r_N$ with an appropriate boundary condition, as we have already noted. The resulting coupled algebraic equations can be solved by standard computer techniques for matrix inversion or diagonalization. Such a method is an effective one provided (1) the needed matrix elements (involving integrations over \vec{r}) can be conveniently calculated by analytic or numerical methods, and (2) it is not necessary to use too many discrete values of ρ to obtain convergent solutions (i.e., independent of r_N or $\rho_{\text{Min}} \equiv 2\pi/r_N$).

The resolvent method should prove more useful for (1) small perturbations or for (2) cases when the integrations of the matrix elements over ρ , are best performed analytically. It could also prove to be a useful method when these integrals are to be done numerically. [It should be noted that the denominators in an expansion like eq. 1.19 can go to zero (for $s = 0$ and ρ or $\rho' \rightarrow 0$). This problem can be eliminated by reordering the expansion in a manner shown by Yoon, Deutch, and Freed [9] corresponding to a total-time-ordered cumulant or projection operator procedure.]

Actually, while these methods have proved very useful when applied to problems involving rotational diffusion (e.g., the triplet initial CIDEP mechanism [6,10]), except for perturbation-type approaches, they have yet to be extensively applied to problems involving translational diffusion (e.g., the radical-pair mechanism).

1.4 Finite difference method

We now turn our attention to finite-difference methods, which have been extensively employed in numerical solutions.

The finite difference solution of the diffusion equation amounts to first letting $\hat{p}(r,t) \equiv rp(r,t)$ so that

$$\frac{\partial \hat{p}(r,t)}{\partial t} = D \frac{\partial^2 \hat{p}(r,t)}{\partial r^2} \quad (1.27)$$

and then to let

$$\frac{\partial \hat{p}(r,t)}{\partial r^2} = \frac{1}{\Delta r^2} [\hat{p}(r-\Delta r,t) - 2\hat{p}(r,t) + \hat{p}(r+\Delta r,t)] \quad (1.28)$$

where we have used the standard mean difference form for the second derivative in terms of the radial increment Δr [6]. This application of the finite difference technique is essentially equivalent to transforming the continuous diffusion equation into a discrete Master equation involving a transition-probability matrix \underline{W} , coupling $p(r,t)$ between discrete values $p(r_0+j\Delta r,t)$ where $j = 0, 1, 2, \dots, N$. These discrete values form a column vector \underline{p} . Thus

$$D \frac{\partial^2 \hat{p}}{\partial r^2} \rightarrow \underline{W} \underline{\hat{p}} \quad (1.29)$$

and the discrete Master equation becomes:

$$\frac{\partial}{\partial t} \underline{\hat{p}} = \underline{W} \underline{\hat{p}} \quad (1.29')$$

with Laplace transform:

$$\underline{\hat{p}}(r,s) = [s - \underline{W}]^{-1} \underline{\hat{p}}(r,t=0) \quad (1.30)$$

which can be solved by straightforward matrix diagonalization or inversion methods, once \underline{W} is specified [see below]. We now have, by comparison of eqs. 1.28 and 1.29, that:

$$W_{j,j-1} = W_{j-1,j} = D/\Delta r^2 \quad (1.31a)$$

$$W_{j,j} = -2D/\Delta r^2 \quad (1.31b)$$

and this corresponds to a tri-diagonal matrix, which is easily solved. Note that $W_{j,j-1}$ is the transition probability from the $j-1$ box (at r_{j-1}) to the j th box (at r_j).

We must also be careful to specify boundary conditions. The reflecting-wall boundary condition at d , the distance of closest approach, is just:

$$\partial p(r,t)/\partial r|_{r=d} = 0 \quad (1.32a)$$

or

$$\partial \hat{p}(r,t) / \partial r \Big|_{r=d} = \hat{p}(d,t) / d \tag{1.32b}$$

which, in finite difference notation, becomes:

$$[\hat{p}(d+\Delta r,t) - \hat{p}(d-\Delta r,t)] / 2\Delta r = \hat{p}(d,t) / d \tag{1.33}$$

This means, that at the boundary we have

$$W_{0,0} = -2D / \Delta r^2 (1 + \Delta r / d) \tag{1.34a}$$

$$W_{0,1} = 2D / \Delta r^2 \tag{1.34b}$$

when eq. 1.33 is used to eliminate the $\hat{p}(d-\Delta r,t)$ term that would otherwise appear in eq. 1.28.

Now, in principle, we want solutions over the whole region $d < r < \infty$; but in order to make them tractable, we require a finite outer limit $r_N = d + N\Delta r$. A very useful boundary condition at r_N , which yields convergent solutions (for r_N large enough), even as $t \rightarrow \infty$ is the "collecting wall" boundary condition. This amounts to letting $W_{N-1,N} = 0$, so the particles (or radical-pairs) collect at r_N and cannot diffuse back. Then the conservation of probability condition requires that $W_{N,N} = 0$ and $W_{N,N-1} = 2D / \Delta r^2$ as well. This conservation of probability condition may be stated as:

$$\int_d^\infty \frac{\partial \hat{p}(r,t)}{\partial t} r dr = D \int_d^\infty \frac{\partial^2 \hat{p}}{\partial r^2} r dr = 0 \tag{1.35}$$

or in finite difference notation where:

$$\frac{\partial}{\partial t} \hat{p} = \underline{W} \hat{p} = \underline{0} \tag{1.36}$$

as:

$$\sum_{i=0}^N V(i) W_{i,j} = 0 \quad \text{for } j = 0, 1, \dots, N \tag{1.37}$$

where $r dr \rightarrow V(i)$. That is, the weighted sum of elements of \underline{W} for each column must be zero. In particular, we have:

$$V(0) = d\Delta r / 2 \tag{1.38a}$$

$$V(i) = r_i \Delta r \tag{1.38b}$$

$$V(N) = r_N \Delta r / 2 \tag{1.38c}$$

It is often useful to distinguish two regions of space (i) $d \leq r < r_M$ and (ii) $r_M < r \leq r_N$, such that fine graining in

Δr is required in region (i) to properly account for particle interactions, while much coarser graining in Δr may be utilized in region (ii) corresponding to large separations. One takes Δr in (ii) as f times larger than that of the former region (where $f \sim 10$ to 100). Then eqs. 1.38 become:

$$V(0) = d\Delta r/2 \quad (1.39a)$$

$$V(i) = r_i \Delta r \quad \text{for } 0 < i < M \quad (1.39b)$$

$$V(M) = r_M(1+f)\Delta r/2 \quad (1.39c)$$

$$V(i) = r_i f \Delta r \quad \text{for } M < i < N \quad (1.39d)$$

$$V(N) = r_N f \Delta r/2 \quad (1.39e)$$

The matrix elements of \underline{W} are again given as in eq. 1.31 for $r_i < r_M$. For $r_i > r_M$, they can be obtained from the elements of eq. 1.31 by dividing by f^2 . The M th row is determined by the conservation of probability eq. 1.37 with the $V(i)$'s of eq. 1.39, giving:

$$W_{M,M-1} = [2/(1+f)](D/\Delta r^2) \quad (1.40a)$$

$$W_{M,M} = -(2/f)(D/\Delta r^2) \quad (1.40b)$$

$$W_{M,M+1} = [2/(1+f)f](D/\Delta r^2) \quad (1.40c)$$

So far, this procedure will merely give numerical solutions to the diffusion equation whose analytic solution is known (e.g., eq. 1.6). We, therefore, consider the new features, such as reactivity and potentials of interaction. Rather than introducing reactivity by an inner boundary condition like eq. 1.9, it is more convenient to explicitly include the effects of a finite reactivity upon radical contact by adding to the diffusion equation a term:

$$\left. \frac{dP}{dt} \right]_{\text{rxn}} = -k(r)p(r,t) \quad (1.41a)$$

where $k(r)$ plays the role of a first-order chemical rate constant. One may use a variety of forms for the functional dependence of $k(r)$ on r . Usually, the simple form:

$$k(r_i) = k\delta_{i,0} \quad (1.41b)$$

has been used, where k is a constant. This represents a "sphere of influence" for the colliding radicals extending from d to $d+\Delta r_k$ with $\Delta r_k = \Delta r$. The effect of this reaction, then, is explicitly included in an augmented \underline{W} matrix. It will be seen below that

this form leads to the following result for Λ , the fractional probability of reaction:

$$\Lambda = k\tau_1/(1 + k\tau_1) \quad (1.42)$$

with

$$\tau_1 = d\Delta r_k/D \quad (1.42')$$

the characteristic "lifetime" of the interacting pair. One may rewrite $\tau_1^{-1} \equiv 4\pi Dd/\Delta V$ where ΔV is the "reaction volume." A comparison of this result with that from [8] yields $\bar{k} \rightarrow k\Delta r_k$.

We now consider the inclusion of the interactive potential $U(r)$ in the form of eq. 1.12. It is rather easy to deal with this new term in the finite difference method. We first define a function $F(r)$ by

$$F(r)\hat{e}_r \equiv (1/kT)\vec{\nabla}U(r) = (1/kT)[\partial U(r)/\partial r]\hat{e}_r \quad (1.43)$$

where $F(r)$ plays the role of the force (but in units of inverse length) in the radial direction represented by unit vector \hat{e}_r . Equation 1.27 now becomes:

$$\frac{\partial \hat{p}(r,t)}{\partial t} = D \frac{\partial^2 \hat{p}(r,t)}{\partial r^2} + \frac{D}{r} \frac{\partial}{\partial r} [\hat{F}(r)\hat{p}(r,t)] \quad (1.44)$$

with $\hat{F}(r) \equiv rF(r)$. The effect of this force is thus to introduce new terms into the \underline{W} matrix when the finite difference approach is employed, i.e.,

$$\frac{\partial}{\partial r} [\hat{F}(r)\hat{p}(r,t)] \rightarrow \frac{\hat{F}(r-\Delta r)\hat{p}(r-\Delta r,t) - \hat{F}(r+\Delta r)\hat{p}(r+\Delta r,t)}{2\Delta r} \quad (1.45)$$

We summarize the additional contributions to \underline{W} :

$$D^{-1}W_{0,0}^F = r_1 F(1)/\Delta r \quad (1.46a)$$

$$D^{-1}W_{0,1}^F = F(0)/\Delta r \quad (1.46b)$$

$$D^{-1}W_{j,j-1}^F = -F(j)/2\Delta r \quad 0 < j < M \quad (1.46c)$$

$$D^{-1}W_{j,j}^F = (2\Delta r)^{-1} [F(j+1)r_{j+1}/r_j - F(j-1)r_{j-1}/r_j] \quad 0 < j < M \quad (1.46d)$$

$$D^{-1}W_{j,j+1}^F = F(j)/2\Delta r \quad 0 < j < M \quad (1.46e)$$

$$D^{-1}W_{M,M-1}^F = -F(M)/\Delta r(1+f) \quad (1.46f)$$

$$D^{-1}W_{M,M}^F = -F(M-1)r_{M-1}/r_M \Delta r(1+f) \quad (1.46g)$$

$$D^{-1} W_{M,M+1}^F = 0 \quad (1.46h)$$

when one chooses r_M such that for $r > r_M$, $U(r) = 0$. Note that these equations are obtained by applying the conservation of probability condition eq. 1.37 wherever necessary. (Note that now $W_{i,j}$ in eq. 1.37 includes the additional terms due to the forces [6,11].) It should be clear, from the concept of \underline{W} as a transition-probability matrix, that we require Δr to be small enough so the off-diagonal elements of \underline{W} are nonnegative, while the diagonal elements of \underline{W} must be nonpositive. An inspection of these elements leads to the sufficiency condition that:

$$\Delta r < |2/F(j)| \quad (1.47)$$

where, usually $|F(0)|$ is the largest of the $F(j)$'s. The solutions may now be obtained by matrix inversion or by diagonalization. It is possible to symmetrize this matrix by the transformation:

$$\tilde{W} \equiv \underline{S} \underline{W} \underline{S}^{-1} \quad (1.48)$$

where \underline{S} is the diagonal matrix whose matrix elements are:

$$S_{00} = 1 \quad (1.49a)$$

$$S_{ii} = S_{i-1,i-1} \sqrt{W_{i-1,i}/W_{i,i-1}} \quad i > 0 \quad (1.49b)$$

$$(S^{-1})_{ii} = (S_{ii})^{-1} \quad (1.49c)$$

It is, thus, necessary to have $W_{i-1,i}/W_{i,i-1} > 0$, so one must let $W_{N-1,N} > 0$, but a value of $W_{N-1,N}/W_{N,N-1} < 10^{-10}$ is sufficient [11].

One may then diagonalize \tilde{W} with a real orthogonal transformation represented by the matrix \underline{O} such that [11]:

$$\underline{w} = \underline{O} \tilde{W} \underline{O}^{tr} = \underline{O} \underline{S} \underline{W} \underline{S}^{-1} \underline{O}^{-1} = \underline{T} \underline{W} \underline{T}^{-1} \quad (1.50)$$

where \underline{w} is the diagonal form consisting of real, nonpositive eigenvalues [12]. Then eq. 1.30 becomes:

$$\hat{p}(r,s) = \underline{T}^{-1} [s - \underline{w}]^{-1} \underline{T} \hat{p}(r,0) \quad (1.51a)$$

or

$$\hat{p}(r_1,s) = \sum_{j,k=0}^N \frac{(T^{-1})_{ij}(T)_{jk}}{s - w_{jj}} \hat{p}(r_k,0) \quad (1.51b)$$

so

$$\hat{p}(r_1,t) = \sum_{j,k=0}^N (T^{-1})_{ij} e^{+w_{jj}t} (T)_{jk} \hat{p}(r_k,0) \quad (1.52)$$

Then

$$p(t) \equiv \int_d^\infty r dr \hat{p}(r,t) \rightarrow \sum_{i=0}^N V(i) \hat{p}(r_i,t) \tag{1.53}$$

is readily obtained as a sum of exponentially decaying quantities. In the absence of any chemical reactions, $p(t) = 1$ is the conservation of probability condition. It arises because there must then be one eigenvalue $w_0 = 0$ and this corresponds to the sum:

$$\sum_{i,k=0}^N V(i) (T^{-1})_{i0} T_{0k} \hat{p}(r_k,0) \text{ which must equal } \sum_{k=0}^N V(k) \hat{p}(r_k,0).$$

Thus, we must have

$$V(k) = \sum_i V(i) (T^{-1})_{i0} T_{0k} \text{ or } \frac{V(k)}{T_{0k}} = c \tag{1.54a}$$

independent of k from which it follows (using $T^{-1}T = \underline{1}$) that

$$\sum_i V(i) T_{ij}^{-1} = c \delta_{0,j} \tag{1.54b}$$

Now let us consider the limit $t \rightarrow \infty$. Then for

$$w_{00} = 0 \text{ and } w_{jj} < 0 \text{ for } j \neq 0$$

we get

$$\lim_{t \rightarrow \infty} \hat{p}(r_i,t) = \sum_{k=0}^N (T^{-1})_{i0} T_{0k} \hat{p}(r_k,0) \tag{1.55}$$

But by eqs. 1.51 and 1.52, this is easily seen to be equivalent to taking $\lim_{s \rightarrow 0} s \hat{p}(r_i,s)$, since, in this limit, only the terms

involving the zero eigenvalues of \underline{w} persist. In general then, for any matrix \underline{A} (which is time independent but may be complex) and which has an eigenvalue spectrum a_j , such that $\text{Re} a_j \lesssim 0$, it will follow, given $\underline{f}(t) = \underline{A} \underline{f}(0)$, that

$$\lim_{s \rightarrow 0} s \underline{g}(s) = \lim_{t \rightarrow \infty} \underline{f}(t) \tag{1.56a}$$

where

$$\underline{g}(s) = \int_0^\infty e^{-st} \underline{f}(t) dt \tag{1.56b}$$

Now when there is a chemical reaction occurring at $r = d$, there is no longer complete conservation of probability (unless there is an inner collecting box). This is then replaced by conservation of all particles (or probability) that reach the collecting wall at r_N at $t \rightarrow \infty$, so that we may write

$$\lim_{t \rightarrow \infty} p(t) = \lim_{t \rightarrow \infty} V(N) \hat{p}(r_N, t) = \lim_{s \rightarrow 0} sV(N) \hat{p}(r_N, s) \quad (1.57)$$

It is interesting to ask about the relationship between solutions such as eqs. 1.51 or 1.52 and eigenfunction expansion methods. The diagonalization of \underline{W} will yield eigenfunctions corresponding to linear combinations of the basis vectors: $|r_i\rangle$ representing the finite grid points in the finite difference method. Each linear combination must correspond to one of the Bessel-function-type eigenfunction chosen for the appropriate outer and inner boundary conditions (including the reactivities). In particular, a finite outer wall at r_N will mean discrete values of ρ such that $\rho_{\min} \sim 2\pi/r_N$. But because of the discreteness of the space we now also have a $\rho_{\max} \sim \pi/\Delta r$ (i.e., an upper cutoff to the allowed wave-vectors).

1.5 Interaction potentials

A) Ionic interactions. A convenient way to represent spin-independent Coulombic forces between charged radicals in ionic solution is to use the usual Debye formulas. Thus, one may write:

$$U(r) = (e^2 Z_a Z_b / \epsilon r) [e^{-\kappa(r-d)} / (1 + \kappa d)] \quad (1.58)$$

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

$$\kappa^2 = (4\pi e^2 / \epsilon kT) \sum_i n_i Z_i^2 \quad (1.59)$$

where ϵ is the dielectric constant and n_i is the number density of the i th type of particle of charge Z_i .

One finds [6] that the effect on the reactivity Λ is merely to require

$$\tau_1^{-1} = \tau_{1,u}^{-1} f^* \exp[U(d)/kT] \quad (1.60a)$$

where

$$(f^*)^{-1} = d \int_d^\infty \exp[U(r)/kT] dr / r^2 \quad (1.60b)$$

and $\tau_{1,u}$ is the value for the uncharged radicals given by eq. 1.42.

B) Pair correlation functions. One can show that $U(r)$ is the potential of averaged forces between the spin-bearing molecules. Thus, we may obtain $U(r)$ from the pair-correlation function $g(r)$, i.e.,

$$\ln g(r) \equiv -U(r)/kT \quad (1.61)$$

so that one has from eq. 1.43

$$F(r) = - \frac{\partial \ln g(r)}{\partial r} \quad (1.62)$$

When these expressions are incorporated into eq. 1.12, then in the limit $t \rightarrow \infty$, $p(\vec{R}; \vec{r}, t)$ will yield the equilibrium $g(r)$, while, for finite times, $-F(r)\hat{e}_{\vec{r}}$ is the driving force acting to restore this equilibrium. The Debye-Hückel formula, eq. 1.58, which includes charge-shielding by the solvent, is only one example. One is able to use pair-correlation functions $g(r)$ obtained from theories of equilibrium statistical mechanics or even from computer dynamics calculations, since for the finite difference method, it is sufficient to have numerical solutions to $g(r)$. An analysis of $p(\vec{R}; \vec{r}, t)$ for hard-sphere potentials appropriate for liquid ethane is given by Hwang and Freed [11] utilizing the finite difference approach.

2. THE STOCHASTIC LIOUVILLE EQUATION: CIDNP AND CIDEP

2.1 Stochastic Liouville equation

The most general form of the stochastic Liouville equation appropriate for the relative diffusion of two spin-bearing molecules, which includes the spin dynamics, has been derived by Hwang and Freed [13] and is given in terms of a position-dependent, spin density matrix $\rho(\vec{r}, t)$:

$$\frac{\partial \rho(\vec{r}, t)}{\partial t} = -iH^{\times}(\vec{r})\rho(\vec{r}, t) + D\Gamma_{\vec{r}}\rho(\vec{r}, t) + DT_{\vec{r}}\rho(\vec{r}, t) + K_{\vec{r}}\rho(\vec{r}, t) \quad (2.1)$$

Here $H^{\times}(\vec{r})$ is the Liouville operator associated with the spin Hamiltonian $H(\vec{r})$ (i.e., for any two operators A and B, $A^{\times}B \equiv [A, B]$). Also, $\Gamma_{\vec{r}}$ is the diffusion operator of the previous section. The term $T_{\vec{r}}$ is given by:

$$T_{\vec{r}} \equiv \frac{1}{2kT} \vec{\nabla}_{\vec{r}} \cdot [(\vec{\nabla}_{\vec{r}} H^{\dagger}(\vec{r}))\rho(\vec{r}, t)] \quad (2.2)$$

where $H^{\dagger}(\vec{r})$ is the anti-commutator form (i.e., $A^{\dagger}B \equiv [A, B]_{+} = AB + BA$). This term gives an effective spin-dependent force which is to be included into the diffusion. It represents the back-reaction of the spins, whose Hamiltonian depends on \vec{r} , onto the diffusional process. In the high-temperature limit (i.e., $|H|/kT \ll 1$) it is shown to be associated with relaxation of the spins to thermal equilibrium. Equation 2.1 may be derived by

first writing the quantum mechanical Hamiltonian equation of motion for the complete liquid and then passing to the semi-classical limit, where the nuclear motions become classical while the spin systems remain quantum mechanical. Then the relative nuclear motions are assumed to obey simple Brownian motion. [In fact, more generally, eq. 2.1 may be interpreted such that the electronic spin and orbital states (as well as nuclear spin states) are treated in terms of a quantum-mechanical density matrix, while the nuclear motions are described by a classical probability distribution function.] The density matrix $\rho(\vec{r}, t)$ then includes both the properties of a spin-density matrix and the classical $p(\vec{r}, t)$ for the relative diffusion. A more complete discussion of this is given by Hwang and Freed [13].

In eq. 2.1, the operator K is introduced phenomenologically, when needed, to represent reactivities for the radical pair. Note that when the interacting molecules have no spin, then eq. 2.1 reduces to the diffusion equation for $p(\vec{r}, t)$ discussed in Sect. 1 (cf. eq. 1.1 or 1.12).

When we deal with CIDEP and CIDNP, the important quantities we need are: (1) the total probability function:

$$P(\vec{r}, t) = \text{Tr} \rho(\vec{r}, t) \quad (2.3a)$$

or

$$P(t) = \int d^3\vec{r} P(\vec{r}, t) \quad (2.3b)$$

Also

$$\rho(t) = \int d^3\vec{r} \rho(\vec{r}, t) \quad (2.3c)$$

[where $P(\vec{r}, t) = p(\vec{r}, t)$] and Tr implies a trace over spin states, and the time-dependent polarization of radical a, given by:

$$P_a(\vec{r}, t) \equiv -2\text{Tr}\{\rho(\vec{r}, t) S_{az}\} \quad (2.4a)$$

or

$$P_a(t) \equiv \int d^3\vec{r} P_a(\vec{r}, t) \quad (2.4b)$$

i.e., the difference in populations between spin up and spin down (the sign convention yields positive equilibrium polarizations P_{eq}). The quantity $P_a(t)$ is of fundamental importance for CIDEP, while the quantity:

$$F(t) \equiv 1 - P(t) \quad (2.5)$$

is of fundamental importance for CIDNP.

We will, as in Sect. 1, assume only r -dependent terms in $U(r)$ and $H(r)$, and let $\hat{\rho}(r, t) \equiv r\rho(r, t)$. Then, again using Laplace transforms, we have:

$$\begin{aligned} \hat{s}\hat{\rho}(\mathbf{r},s) - \hat{\rho}(\mathbf{r},0) = & -iH^{\times}(\mathbf{r})\hat{\rho}(\mathbf{r},s) + D \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \hat{F}(\mathbf{r})^T \right] \hat{\rho}(\mathbf{r},s) \\ & + K_r \hat{\rho}(\mathbf{r},s) \end{aligned} \quad (2.6)$$

where

$$\hat{F}(\mathbf{r})^T \equiv \hat{F}(\mathbf{r}) + \frac{1}{2kT} \frac{\partial H^{\dagger}(\mathbf{r})}{\partial r} \quad (2.7)$$

We need only solve this equation by straightforward generalizations of the methods employed in Section 1, i.e., eigenfunction expansion procedures or finite differences. We follow [6] and employ finite difference below in discussing the radical pair mechanism. Also, for simplicity, we initially let $\hat{F}(\mathbf{r})^T = \hat{F}(\mathbf{r})$, so, if not for the spin Hamiltonian term $H^{\times}(\mathbf{r})$, we would just have the diffusion problem of Section 1.

2.2 Finite difference method

How do we now introduce the effects of $H^{\times}(\mathbf{r})$? Recall that for each finite-difference value r_i we would have a value of $\hat{\rho}(r_i,s) = \text{Tr}\hat{\rho}(r_i,s)$. Thus, for each r_i we have a matrix of values of $\hat{\rho}(r_i,s)$. Let $\hat{\rho}(r_i,t)$ be represented by an L dimensional matrix, so there are L^2 matrix elements. Then the vector space in which $\hat{\rho}(s)$ is defined will be an $L^2 \times (N+1)$ dimensional space formed from the direct product of the L^2 spin-superspace and the $N+1$ dimensional space spanned by the r_i for $0 \leq i \leq N$. The complete solution will now become a matrix equation in this space:

$$[s\underline{\underline{1}} - \underline{\underline{K}}' - \underline{\underline{W}}' + i\underline{\underline{\Omega}}]\hat{\rho}(s) = \hat{\rho}(0) \quad (2.8)$$

The $\underline{\underline{W}}'$ matrix is just the $\underline{\underline{W}}$ matrix of Section 1, but with each element replaced by the product of that element and an $L^2 \times L^2$ unit matrix, since $D\nabla_r$ is independent of spin. The $\underline{\underline{\Omega}}$ matrix represents the matrix elements of $H^{\times}(\mathbf{r})$. It consists of blocks of $L^2 \times L^2$ matrices for each value of r_i ; i.e., it has a block diagonal form. The $\underline{\underline{K}}'$ matrix includes the effects of the reactivities.

One solves the matrix eq. 2.8 for the elements of $\hat{\rho}(s)$ or $\hat{\rho}(r_i,s)$. This could be performed by diagonalization techniques as discussed in Section 1. Instead, let us consider the long time limit so that it is only necessary to consider the $s \rightarrow 0$ case, i.e., we solve for

$$P \equiv \lim_{t \rightarrow \infty} P(t) = \lim_{s \rightarrow 0} sP(s) \quad (2.9)$$

and

$$P_a^\infty \equiv \lim_{t \rightarrow \infty} P_a(t) = \lim_{s \rightarrow 0} sP_a(s) \quad (2.10)$$

This is accomplished by solving eq. 2.8 for a value of s , small enough that $\hat{p}(s)$ has converted to its limiting value. (Note that the eigenvalues of the matrix $\underline{W}' + \underline{K}' - i\underline{\Omega}$ will be complex: the real nonpositive contributions coming from $\underline{W}' + \underline{K}'$ and the imaginary parts from $-i\underline{\Omega}$.)

2.3 Density matrix elements and spin Hamiltonian

Let us now consider the particular matrix elements of ρ that are required. We first express them in terms of the standard singlet and triplet states of the radical pair, using S , T_0 , and T_\pm , while ρ_{AB} refers to the AB th matrix element of ρ .

Then

$$P(t) = \rho_{SS}(t) + \rho_{T_0T_0}(t) + \rho_{T_+T_+}(t) + \rho_{T_-T_-}(t) \quad (2.11)$$

Now we rewrite $2S_{az} = (S_{az} - S_{bz}) + (S_{az} + S_{bz})$. Then we easily find that

$$P_a(t) = -[\rho_{ST_0}(t) + \rho_{T_0S}(t)] + [\rho_{T_-T_-}(t) - \rho_{T_+T_+}(t)] \quad (2.12a)$$

and

$$P_b(t) = -2\text{Tr}\{\rho(t)S_{bz}\} = [\rho_{ST_0}(t) + \rho_{T_0S}(t)] + [\rho_{T_-T_-}(t) - \rho_{T_+T_+}(t)] \quad (2.12b)$$

Let us now consider the spin-Hamiltonian $H(r)$ for the interaction of radical pair A-B.

We write this as:

$$H(r) = H^0(r) + H' \quad (2.13)$$

where $H^0(r)$ is diagonal in the singlet-triplet representation, while the off-diagonal part, H' of $H(r)$ is independent of r . Then we have

$$H^0(r) = \frac{1}{2} (g_a + g_b) \beta_e \hbar^{-1} B_0 (S_{az} + S_{bz}) + \frac{1}{2} \left(\sum_j^a A_j \vec{I}_j + \sum_j^b A_k \vec{I}_k \right) \times \cdot (\vec{S}_a + \vec{S}_b) - J(r) \left(\frac{1}{2} + 2\vec{S}_a \cdot \vec{S}_b \right) \quad (2.14a)$$

$$H' = \frac{1}{2} (g_a - g_b) \beta_e \hbar^{-1} B_0 (S_{az} - S_{bz}) + \frac{1}{2} \left(\sum_j^a A_j \vec{I}_j - \sum_j^b A_k \vec{I}_k \right) \times (\vec{S}_a + \vec{S}_b) \quad (2.14b)$$

Thus H' only includes differences in g -values and hyperfine energies between the two interacting radicals as discussed in previous chapters. $J(r)$ is the exchange interaction between radicals which depends explicitly on r .

We will now simplify the analysis to high-field experiments. Thus we only need consider the $A_j I_{jz} S_{az}$ -type hyperfine components. As a result of this, only the S and T_0 states are found to couple to give induced polarizations (except when the initial triplet polarization is operative [6,10]). Thus, for the high-field radical-pair mechanism, we can neglect the $\rho_{T_{\pm}T_{\pm}}(t)$ in eqs. 2.12. We can now use the eqs. 2.14 to find the matrix elements of $H(r) \times \rho$ in the subspace defined by the S and T_0 levels. One finds that

$$\begin{pmatrix} [H^x(r)\rho]_{SS} \\ [H^x(r)\rho]_{ST_0} \\ [H^x(r)\rho]_{T_0S} \\ [H^x(r)\rho]_{T_0T_0} \end{pmatrix} = \begin{pmatrix} 0 & -Q & Q & 0 \\ -Q & 2J(r) & 0 & Q \\ Q & 0 & -2J(r) & -Q \\ 0 & Q & -Q & 0 \end{pmatrix} \begin{pmatrix} \rho_{SS} \\ \rho_{ST_0} \\ \rho_{T_0S} \\ \rho_{T_0T_0} \end{pmatrix} \quad (2.15)$$

Here:

$$2Q \equiv (g_a - g_b) \beta_e \hbar^{-1} B_0 + \left(\sum_j^a A_j^a M_j^a - \sum_k^b A_k^b M_k^b \right) \quad (2.16)$$

so $2Q$ is the difference in ESR resonant frequencies between separated radicals A and B. Equation 2.15 thus defines the 4×4 block form of $\underline{\Omega}$ of eq. 2.8 for each value of r_{\perp} . The only r dependence is in $J(r)$. One expects an exponentially decaying exchange interaction, which we write as:

$$J(r) = J_0 \exp[-\lambda(r-d)] \quad (2.17)$$

One also finds that $[H^x \rho]_{T_{+}T_{+}} = [H^x \rho]_{T_{-}T_{-}} = 0$, thus confirming the fact that the T_{\pm} states do not contribute to the polarization process in the high field limit.

2.4 Spin-dependent reactivity

We now consider the superoperator $K(r)$ and its associated matrix \underline{K}' . In particular, we wish to consider a spin selective reaction between the radical pair when in contact. For definiteness, we

assume that only radical pairs in the singlet state may react. Thus, we may introduce equations like eqs. 1.41a and b, but only for singlet states. Since $K(r)$ is phenomenologically introduced, we need to use it in a fashion that is consistent with the properties of the density matrix. It is well known that a decay of diagonal density matrix elements [e.g., $\rho_{SS}(d,t)$], will lead to a lifetime-uncertainty-broadening for associated off-diagonal elements (e.g., $\rho_{ST_0}(d,t)$ and $\rho_{T_0S}(d,t)$ are broadened by the mean of the decay rates of S and T_0 states). These two effects are well represented by writing [2]:

$$K\rho = [-k(r)/2][|S\rangle\langle S|\rho + \rho|S\rangle\langle S|] \equiv [-k(r)/2]|S\rangle\langle S|^{\dagger}\rho \quad (2.18)$$

If we use eq. 1.41b for $k(r)$, then \underline{K}' is completely defined. [Note that, in general, off-diagonal elements ρ_{ij} are not completely independent of the diagonal elements ρ_{ii} and ρ_{jj} , due to the inequality $\text{Tr}(\rho^N)^2 \leq 1$ where $\rho^N \equiv \rho/\text{Tr}\rho$ (which follows from the fact that in diagonal form all elements of ρ^N must be real and positive [14]). This formal requirement is what should be associated with the Heisenberg uncertainty-in-lifetime effect (usually written as $\Delta\omega\Delta t \geq 1$), on ρ_{ij} , $i \neq j$, with eq. 2.18 representing the equality.]

However, it is not necessary to be satisfied simply with a phenomenological treatment of reactivity. This is because we have in eqs. 2.6-2.7 a spin-dependent potential and associated force $(1/2kT)[\partial H^{\dagger}(r)/\partial r] = (1/2kT)(\frac{1}{2} + 2\vec{S}_a \cdot \vec{S}_b)^{\dagger}[\partial J(r)/\partial r]$, which, for singlet reactivity, will lead to bonding attraction of the singlet state but anti-bonding repulsion of the triplet state (cf. Fig. 1). This tells us that eq. 2.6 already includes chemical reactivity for the radical-pair even with the phenomenological $K_r = 0$. This is as it should be, since the spin-dependent Smoluchowski eq. 2.6 has been derived from the complete semi-classical many-body problem including all the interactions. It is then only approximate in (1) its treatment of the surrounding molecules as a simple diffusive background and (2) its coarse-graining-in-time neglect of momentum of the radical-pair, which is equivalent to letting the momentum relax instantaneously. The former ignores solvent structure, while the latter is really inadequate in dealing with strong interactions, although the more complete spin-dependent Fokker-Planck theory including momentum still contains the same spin-dependent potential. Thus, either in the Smoluchowski or Fokker-Planck forms, this theory supplies the spin-dependent, but adiabatic, reactive trajectories, which are determined by Coulomb and exchange interactions. This is referred to as a self-consistent (SC) method, since it requires that the effects of $H(r)$ must appear both in the commutator $H^{\times}(r)$ representing the purely dynamical motions of the spins in eq. 2.6 and the total force $\hat{F}(r)^{\dagger}$ in eq. 2.7. Also note that the anti-commutator $[H^{\dagger}(r)/2kT]$ plays a role formally analogous to the phenomenological $k/2 |S\rangle\langle S|^{\dagger}$ in eq. 2.18.

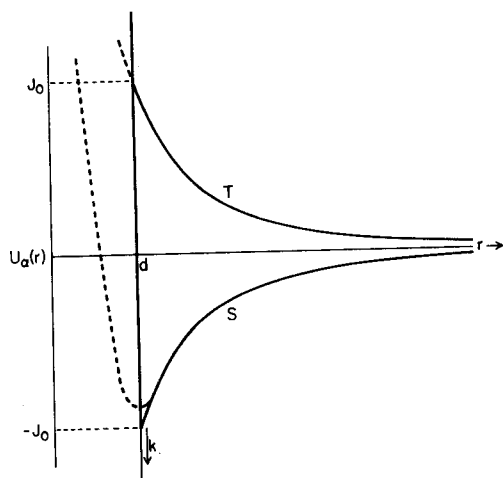


Figure 1. Spin Dependent Potentials $U_\alpha(r)$ as a function of r the interradical separation. The solid curves labeled S and T represent the exchange potentials utilized for singlet and triplet states respectively, with a reflecting wall at $r = d$. The dashed lines represent the usual continuation of the potentials in the absence of a reflecting wall. (By permission from Pedersen and Freed [3].)

We will, in our discussion of specific models below, find that we can approximate the particular SC model based upon Fig. 1 (referred to in [6] as the EFP model), by replacing the $H^+(r)/2kT$ term in eq. 2.6 with a phenomenological

$$K\rho = -k(r) |S\rangle \rho_{SS} \langle S| \quad (2.19)$$

but with $H(r)$ still in the commutator of eq. 2.6. We will call this the ASC model (in [6] it is referred to as the EFA model). We will favor the ASC model in our discussion (partly also for its greater simplicity), while the fully phenomenological form of eq. 2.18 is employed in the original work of ref. [2].

2.5 Initial conditions and transfer factors

It now only remains to specify initial conditions in order to be able to solve eq. 2.6. We will usually consider a radical-pair at some initial separation, r_I . Thus $\rho(r,0) = \rho_0 \delta(r-r_I)/r_I^2$. Thus in the case of pure singlet at $r_I = d$ one has in finite-difference form:

$$\hat{\rho}_{S,S}(r_I,0) = \delta_{i,0}/V(0) \quad (2.20)$$

It follows from the linear homogeneous form of eq. 2.1 (or 2.6) that we can superpose solutions obtained for different initial conditions, to obtain the solution to the problem involving an initial condition, which is itself a linear combination of already solved initial conditions. We refer to this as the superposition principle.

In problems involving random collisions (i.e., RI) in which there are forces between radicals, the diffusion affects the rate of the initial encounter. Thus it is necessary to start the radical-pair (for RI) at a position r_I such that $\hat{F}(r_I)^T \approx 0$. Then, to get around the arbitrariness of such an initial state, we define a transferred polarization, etc., by:

$$P_a^\infty(d_t) \equiv [k_2(r_I)/k_2(d)]P_a^\infty(r_I) = (r_I/d)P_a^\infty(r_I) \quad (2.21)$$

As a result of the effects of the forces between radical-pairs, $P_a^\infty(d_t)$ is not the same as that for a true initial condition of $r_I = d$, since it includes the effects of the forces on the initial approach before contact of the radical-pair. In the case of a finite absorbing wall at $r = r_N$, eq. 2.21 must be rewritten as:

$$P_a^\infty(d_t) \xrightarrow[r_N]{\text{finite}} d^{-1}(r_I^{-1} - r_N^{-1})^{-1}(1 - d/r_N)P_a^\infty(r_I) \quad (2.22)$$

This expression comes about as follows. One has from eqs. 1.10 that $k_2(r_I) \propto r_I/d = t_f(r_I)^{-1}$ (or inversely with the probability of encounter) for diffusional encounters from an infinite medium. The probability that particles separated at r_N will encounter is, however, d/r_N , and since there is an absorbing (or collecting wall at r_N), one must subtract this amount, i.e., $k_2(r_I) \propto 1/[t_f(r_I) - t_f(r_N)] = d^{-1}(r_I^{-1} - r_N^{-1})$. Similarly for $k_2(d_t)$ (neglecting forces) $\propto [1 - t_f(r_N)]^{-1} = (1 - d/r_N)^{-1}$. (See below for a definition of t_f .)

3. RESULTS AND MODEL DEPENDENCE

As we have previously noted, it is possible by numerical methods to obtain solutions for a wide range of models which may not be accessible to analytic solutions. One of the significant findings in the original work [1-6] is that the numerical results (where at $t = 0$ the particles are in contact) may be summarized by a series of relatively simple expressions, and that most of these expressions are model independent.

3.1 CIDNP

Let us first consider CIDNP. We note that Λ , the fractional probability of reaction (for $Q = 0$) of singlet (for singlet

reactivity) may be defined as

$$\Lambda \equiv F_0(S) \quad (3.1)$$

(Note, in this notation the subscript refers to $Q = 0$ and $F(i)$ means i initially.) This fractional probability of reaction includes all re-encounters of the radical-pair, which we shall refer to as the complete collision. We then define:

$$F^* \equiv \lim_{\Lambda \rightarrow 1} F(T_0) = \lim_{\Lambda \rightarrow 1} [F(T_0) - F_0(T_0)] \quad (3.2)$$

since $F_0(T_0) = 0$, so that F^* measures the conversion from triplets to singlets for the whole collision. A set of results that are exact and model independent are:

$$-[F(S) - F_0(S)] = -[F(S) - \Lambda] = (1 - \Lambda)F(T_0) \quad (3.3)$$

i.e., the net decrease in reaction for pure singlets per collision due to $Q \neq 0$ is just the probability a singlet does not react for $Q = 0$ (i.e., $1 - \Lambda$) times the probability pure triplets do ultimately react because of mixing of triplets and singlets (Q -mixing). The superposition principle may then be applied to obtain the result for random initial condition (i.e., equal amounts of singlet and triplet):

$$F(RI) = \frac{1}{2} [F(S) + F(T_0)] \quad (3.4)$$

then eq. 3.3 may be rewritten as:

$$[F(RI) - F_0(RI)]/F_0(RI) = F(T_0) \quad (3.5)$$

where $F_0(RI) = \frac{1}{2}\Lambda$. The role of the parameter F^* appears in the exact relation:

$$F(T_0) = \Lambda F^* [1 + F^*(1 - \Lambda)]^{-1} \quad (3.6)$$

so that eqs. 3.3 and 3.5 become:

$$F(S) = \Lambda [1 + F^*(1 - \Lambda)]^{-1} \quad (3.7)$$

and

$$F(RI) = \frac{1}{2} \Lambda (1 + F^*) [1 + F^*(1 - \Lambda)]^{-1} \quad (3.8)$$

[Note that these expressions are easily converted for T_0 reactivity by interconverting $F(S)$ and $F(T_0)$ in all the definitions and expressions above. The T_{\pm} states are still treated separately and independently in the high field case.] The triplet or singlet initial cases are of interest for CIDNP due to recombination of a geminate radical pair which were originally formed in the triplet or singlet state. The random initial case is appropriate for a

radical-pair which experience a random encounter. One may combine the result of eq. 3.8 with the usual steady-state bimolecular rate of encounters, eq. 1.10, to obtain the effective bimolecular spin-dependent reaction rate (for singlets) of:

$$k_f^S = F(RI)k_2(d) \quad (3.9)$$

Again, it is interesting to note that these above results are all model independent and exact as demonstrated by the numerical results. It is only in the precise forms of Λ and F^* that there is model dependence. Note that typically Λ obeys the form of eq. 1.42 but with τ_1 given by eq. 1.42a for no interaction potentials, while it is given by eq. 1.60 for interaction potentials (e.g., Coulombic interactions). We have found that for a model, which corresponds to an apparent space-dependent diffusion-coefficient [i.e., the replacement of D by $D(r) = D(1 - a/r)$] and based on Oseen's tensor, one obtains eq. 1.60, but with f^* replaced by \tilde{f}^* :

$$(\tilde{f}^*)^{-1} = d \int_d^\infty \exp[U(r)/kT] [r^2(1 - a/r)]^{-1} dr \quad (3.10)$$

Equation 1.60 also applies for models involving the spin-dependent exchange interaction, provided $|KJ_0/kT|$ is not much greater than unity (see below).

We now consider F^* . In the case of small values of $J_0d/\lambda D$ it is found to be independent of $J(r)$ and a function only of the dimensionless variable Qd^2/D . (See [6] for a discussion of the solutions to eq. 2.6 in terms of dimensionless variables.) In the interaction-free case, it is then possible to obtain good agreement with the numerical results with the analytic form:

$$F^* \approx \frac{\frac{1}{2} \{1 + \frac{1}{2} \ln[1 + (Qd^2/D)^{\frac{1}{2}}]\} (Qd^2/D)^{\frac{1}{2}}}{1 + \frac{1}{2} \{1 + \frac{1}{2} \ln[1 + (Qd^2/D)^{\frac{1}{2}}]\} (Qd^2/D)^{\frac{1}{2}}} \quad (3.11)$$

as demonstrated in Table 1. The simple form $F^* \sim \frac{1}{2}(Qd^2/D)^{\frac{1}{2}}$, valid for $(Qd^2/D)^{\frac{1}{2}} \ll 1$, confirms the important role of the re-encounter mechanism as discussed in the previous chapters. A likely interpretation of the logarithmic term in eq. 3.11 in terms of the "initial encounter" mechanism is presented below. Note that in the asymptotic limit: $\lim_{(Qd^2/D) \rightarrow \infty} F^* = 1$, i.e., with infinitely rapid

Q-mixing all the initially triplet spins are completely converted to singlet states and react (cf. eq. 3.2). [Note a simpler form of eq. 3.11 (Table 1) was slightly misprinted in [6].]

This, then, is an example of how numerical results can be converted to useful approximate analytic forms. In this, it is

Table 1. Dependence of F^* on (Qd^2/D) for small values of $J(r)$

Qd^2/D	F^{*a} (numerical)	F^{*b} (theory)	F^{*c} (simple)
1.6×10^{-3}	0.019863	0.01998	0.019608
1.6×10^{-2}	0.067974	0.06281	0.059484
1.6×10^{-1}	0.20099	0.18940	0.16667
1.6	0.49620	0.47117	0.38743
1.6×10^1	0.78435	0.78305	0.66667
1.6×10^2	0.93588	0.93585	0.86347
1.6×10^5	1.0000	0.99875	0.99503

a) Results computed by finite differences.

b) Results predicted by eq. 3.11

c) Results predicted by simple form $F^* = \frac{1}{2}(Qd^2/D)^{1/2} / [1 + \frac{1}{2}(Qd^2/D)^{1/2}]$.

useful to be guided by (1) analytic solutions to simpler models; and (2) consideration of proper limiting cases.

The effects of Debye-Hückel-type Coulombic forces on F^* may be approximately represented by letting

$$F^* \approx F_u^* f_u^* (1 + \delta) \quad (3.12)$$

where F_u^* are the results obtained for uncharged radicals and $\delta \approx \frac{1}{4}$ for attraction and $0 \leq \delta \leq \frac{1}{4}$ for repulsion (with $Q \sim 10^8 \text{ sec}^{-1}$, $D \sim 10^{-5} \text{ cm}^2/\text{sec}$), but more generally δ is somewhat sensitive to Q and kd . They are given in graphs in [6]. Note that from the simple form of $F^* \approx \frac{1}{2}(Qd^2/D)^{1/2}$ valid for $(Qd^2/D) \ll 1$ [cf. eq. 3.11], one might expect to replace the d by an effective interaction distance, f^*d (cf. eq. 1.60b), so that $F^* \approx f^*F_u^*$. Thus the small $\delta \neq 0$ in eq. 3.12 reflects the long-range effect on the relative diffusive motion affecting the re-encounter dynamics and Q -mixing. This illustrates an important difference between CIDNP and the usual models of liquid-state reaction kinetics.

When Oseen's tensor is introduced, the effects of F^* are somewhat more complex, but are discussed in detail in [5]. In general the ratio F_{OS}^*/F_N^* ($OS = \text{Oseen}$, $N = \text{without Oseen tensor}$), range from ca. 1/2 to 1.3. Again, to a first approximation, one should replace d in eq. 3.11 by \tilde{f}^*d , so for small Qd^2/D one expects $F_{OS}^*/F_N^* \approx \tilde{f}^*/f^* \approx \tau_{1,N}/\tau_{1,OS}$.

The above discussion is appropriate for $J_0d/\lambda D \ll 1$. When, however, $J_0d/\lambda D \gtrsim 1$, the results for F^* become weakly dependent upon F^* , tending to reduce it in magnitude. This effect is

roughly expressed by:

$$F_{J=0}^*/F^* \approx 1 + \frac{5}{3} (\lambda d)^{-1} \ln[1 + (J_0 d^2/D) (\lambda d)^{-1}] \ln[1 + (Qd^2/D)^{0.45}] \quad (3.13)$$

The physical picture here is that of an "exchange-volume," i.e., a region extending beyond the contact distance d and satisfying $J(r) > Q$, so that Q -mixing is suppressed. Since it is found that for small Qd^2/D the effects of re-encounters after longer separations are needed for Q -mixing, this excluded volume has less of an effect for small Qd^2/D . The effects of Oseen's tensor and shielded Coulombic attractions are also modified by appreciable values of $J_0 d/\lambda D$. Again one finds enhanced effects for larger Qd^2/D (cf. [5]). Also, one should note how, by numerical methods, it is possible to calculate the simultaneous effects of these various interactions. It is then frequently possible to interpret them in terms of one's understanding of the physical models.

Another important property of the CIDNP solutions is given by the transfer factor t_f , defined as:

$$t_f \equiv \Delta F(RI, r_I) / \Delta F(RI, d) \quad (3.14)$$

where

$$\Delta F(RI, r_I) = F(RI) - F_0(RI) \quad (3.15)$$

with an initial separation of $r_I \geq d$. For a simple diffusive model,

$$t_f = d/r_I \quad (3.16)$$

Also, t_f is the probability that two particles initially separated by r_I will encounter at least once at $r = d$. That eq. 3.14 is equivalent to this simple definition, follows from the fact that for random initial condition, the CIDNP process only starts upon initial encounter. Equation 3.14 may be usefully employed with eq. 3.8. (The results for singlet and triplet initial have been discussed in [6].) When (shielded) Coulombic forces are introduced, then one finds quite a good fit to:

$$t_f = 1 - f^*/f^*(r_I) \quad (3.17a)$$

where

$$f^*(r_I)^{-1} = d \int_d^{r_I} \exp[U(r)/kT] (dr/r^2) \quad (3.17b)$$

so that

$$f^* = \lim_{r_I \rightarrow \infty} f^*(r_I) \quad (3.18)$$

Now one way of looking at $t_f(r_I)$ is that it must equal the ratio of the rates of new bimolecular encounters at separations of r_I versus d . That is, $t_f(r_I) = k_2(d)/k_2(r_I)$ which is easily shown to be in agreement with eq. 3.17. Similarly, with Oseen's tensor one expects $t_f = 1 - \tilde{f}^*/\tilde{f}^*(r_I)$ by analogy with eq. 3.7 and using eq. 3.10.

3.2 CIDEP polarizations

For CIDEP we again obtain a series of exact expressions:

$$P_a^\infty(\text{RI})/F(\text{RI}) = -P_{a,k=0}^\infty(S) = P_{a,k=0}^\infty(T_0) \quad (3.19)$$

where the subscript $k = 0$ indicates no chemical reaction. This is easily rearranged with the use of eqs. 3.3 and 3.4 to give

$$P_a^\infty(\text{RI}) = \frac{1}{2} \Lambda [1 + F(T_0)] P_{a,k=0}^\infty(T_0) \quad (3.20)$$

Also one finds

$$P_a^\infty(T_0) = (1 + F^*) [1 + (1 - \Lambda) F^*]^{-1} P_{a,k=0}^\infty(T_0) \quad (3.21)$$

and

$$P_a^\infty(S) = (\Lambda - 1) P_{a,k=0}^\infty(T_0) \quad (3.22)$$

Thus, we see that all the CIDEP polarizations are obtained from a knowledge of Λ , F^* , and $P_{a,k=0}^\infty(T_0)$. Again these exact relations are independent of the model. We, therefore, only have to discuss $P_{a,k=0}^\infty(T_0)$ and its model dependences. [Note that these results are based upon using eq. 2.19 for $K(r)$. The results for eq. 2.18 are discussed in [2,6]. They require some modification of the above exact expressions for $k \neq 0$ for smaller values of J_0 . However, small values of J_0 , according to the self-consistent approach, should mean that the spin-dependent reactivity is negligibly small (see also below).]

The numerical results can be incorporated into the approximate form:

$$|P_{a,k=0}^\infty(T_0)| \approx \left(\frac{Qd^2}{D} \right)^\epsilon \frac{2 |J_0| \tau_1(\lambda) + \left[\frac{3}{2} (\lambda d)^{\epsilon'} \right] [2J_0 \tau_1(\lambda)]^2}{1 + [2J_0 \tau_1(\lambda)]^2} \quad (3.23)$$

where

$$\tau_1(\lambda) \approx (d/D\lambda) [1 + (\lambda d)^{-1}] \quad (3.24)$$

and $\epsilon \sim \frac{1}{2}$ for $(Qd^2/D) \leq 0.016$ while $\epsilon' \sim 1$ for $\lambda d \gg 1$ and $(Qd^2/D) \leq 0.016$, but ϵ and ϵ' become smaller as these inequalities

are violated. Also, the sign of $P_{a,k=0}^{\infty}(T_0)$ is determined as follows:

$$\text{Sign}[P_a^{\infty}] = [\text{Sign } Q] \times [\text{Sign } J] \quad (3.25)$$

Note from eq. 3.23 that for large J_0 , P_a^{∞} takes on an asymptotic value:

$$\lim_{J_0 \rightarrow \infty} |P_{a,k=0}^{\infty}(T_0)| \approx \frac{3}{2(\lambda d)^{\epsilon}} (Qd^2/D)^{\epsilon} \quad (3.26)$$

while the maximum value of P_a^{∞} occurs at

$$J_0(\text{max}) \approx [2\tau_1(\lambda)]^{-1} \quad (3.27)$$

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

$$|P_{a,k=0}^{\infty}(T_0)| \approx (Qd^2/D)^{\epsilon} \frac{2|J_0|^{\tau_{1,J}}}{1 + (2J_0^{\tau_{1,J}})^2} \quad (3.28)$$

with

$$\tau_{1,J} \equiv d\Delta r_J/D \quad (3.28a)$$

where Δr_J is the very small extent of the exchange region. The $(Qd^2/D)^{\frac{1}{2}}$ dependence in eqs. 3.26-3.28, for smaller values is indicative of the re-encounter mechanism discussed in the previous chapters. However, for larger values of (Qd^2/D) (e.g., viscous solvents), the required S- T_0 mixing can occur extensively, so one expects the effects of the "complete collision" to be dominated by the initial encounters. This is shown by the expression, valid for small J_0 , which we have found to represent the Q dependence for large Qd^2/D :

$$|P_{a,k=0}^{\infty}(T_0)| \approx 1.18(Qd^2/D)^{\frac{1}{2}} [2J_0\tau_1(\lambda)] \left\{ 1 - \frac{1.56(Qd^2/D)^{\frac{1}{2}}}{1 + 1.56(Qd^2/D)^{\frac{1}{2}}} - \frac{0.8 \ln[1 + \frac{1}{2}(Qd^2/D)^{\frac{1}{2}}]}{1 + 1.6(Qd^2/D)^{(0.48+\delta)} \ln[1 + \frac{1}{2}(Qd^2/D)^{\frac{1}{2}}]} \right\} \quad (3.29)$$

for $|2J_0\tau_1(\lambda)| \ll 1$.

Here δ increases slowly from zero as Qd^2/D becomes ≥ 16 and is larger for smaller λ . This fits the data very well, cf. Table 2. Note that the correction terms include (Qd^2/D) to the first power, which should represent the effects of the initial encounter [see below]. The results for large $J(r)$ are somewhat more complex,

Table 2. Dependence of P_a^∞ on (Qd^2/D) for small values of $J(r)$.^a

Qd^2/D	$r_{ex} = 2 \text{ \AA}^b$	$r_{ex} = 4 \text{ \AA}^c$	$r_{ex} = 8 \text{ \AA}^d$
1.6×10^{-4}	21.4 (21.1)	42.0 (44.0)	97.1 (95.0)
1.6×10^{-3}	64.3 (63.3)	127 (132)	292 (285)
1.6×10^{-2}	169 (170)	331 (355)	761 (766)
1.6×10^{-1}	326 (332)	637 (693)	1436 (1496)
1.6	323 (300)	617 (625)	1290 (1350)
16	163 (159)	280 (332)	466 (716)

- a) Polarizations given as $10^3 \times P_a^\infty$. The first number is the numerical solution, the number in parentheses is from eq. 3.29 but with $\delta = 0$. Also $r_{ex} \equiv \lambda^{-1} 5 \ln 10$.
- b) $2J_0\tau_1(\lambda) = 1.450$.
- c) $2J_0\tau_1(\lambda) = 3.021$.
- d) $2J_0\tau_1(\lambda) = 6.525$.

so we do not reproduce them here. In all cases, however, one finds that

$$\lim_{Q \rightarrow \infty} P_a^\infty = 0 \tag{3.29a}$$

The asymptotic dependence of P_a^∞ with $J_0\tau_1(\lambda) \gg 1$ may be understood in terms of an effective region of polarization. The inner region, where $J(r) > J_0(\max)$, is primarily effective in quenching any polarization by a Heisenberg exchange mechanism; while the desirable or polarization-effective range in $J(r)$, i.e., $J(r) \sim J_0(\max)$, merely moves out farther from r_0 . (Note also that one may consider different functional forms for $J(r)$, but the above results are not very sensitive to such variations [6].)

We may attempt to predict the effects of Coulombic forces on CIDEP polarizations as follows. For $2J_0\tau_1 < 1$ and $(Qd^2/D) \ll 1$, then $P_a^\infty \approx (Qd^2/D)^{1/2} 2J_0\tau_1(\lambda)$. Then, to a first approximation we would let $\tau_1(\lambda)$ have the $f^{-1} \exp[-U(d)/kT]$ dependence that appears in eq. 1.60. [This will not be such a good approximation if λ is small, i.e., a long-range $J(r)$.] Also we would let $d \rightarrow f*d$. This simple analysis would lead to:

$$P_a^\infty / P_{a,u}^\infty \approx \exp[-U(d)/kT] \tag{3.30}$$

which is in accord with the actually calculated trends, although it is not quantitative. In particular [with $r_{ex}/d = 1$ with $r_{ex} \equiv \lambda^{-1} 5 \ln 10$], for attractive forces the calculated result is about 80% of the simple prediction of eq. 3.30 while for repulsive

forces it is about 160-180%. This is as though one should use a $U(r)$ with r a little larger than d in eq. 3.30. As (Qd^2/D) becomes larger, the trends are affected by the changed dependence on this variable. A similar analysis for large $J_0\tau_1(\lambda)$ utilizing eq. 3.26 suggests that for (Qd^2/D) small, P_a^∞ should only depend weakly upon Coulomb forces. The repulsive forces yield an enhancement (typically less than 50%), while attractive forces give reductions by factors up to 3. These effects may again be understood by recognizing that for higher J_0 -values the region of effective polarization moves out to $r > d$ where the Coulomb forces are reduced.

When Oseen's tensor is included, one sees effects which can be rationalized similarly. Thus for small J_0 , $(P_a^\infty)_{OS}/P_a^\infty \approx \tau_{1OS}/\tau_1 \times F_{OS}^*/F^* \sim 1$, while for much larger Qd^2/D , this ratio $\rightarrow f^*/f^*$. The results for high J_0 , show only a small effect, again because the effective region is $r > d$, where Oseen tensor effects are reduced.

3.3 Convergence of the solutions

The above results are based upon obtaining convergence with the finite difference method. One can summarize these conditions as: (1) Δr must be small enough; (2) r_N and r_M must be large enough; and (3) s be small enough that the limit $s \rightarrow 0$ has been achieved. Condition (1) is found to be satisfied if $J(r_i)/J(r_i+\Delta r) = e^{\lambda\Delta r} \lesssim 5$, while (2) for r_M requires that $J(r_M) \ll Q$. Note that a small s implies a large t . That is, consider eqs. 1.51 and 1.52. The limit on $\hat{p}(r_i, s)$ is achieved when $s \ll |w_{\min}|$, where w_{\min} is the smallest non-zero eigenvalue of \underline{W} ; while for $\hat{p}(r_i, t)$ it is achieved when $t^{-1} \ll |w_{\min}|$. Thus, we see that the s and t needed for convergence should be approximately related as $s_{\text{conv}} \sim t_{\text{conv}}^{-1}$. In general, one finds that $s_{\text{conv}} \propto Q$ (provided r_N is sufficiently large). In particular, for CIDEF one has

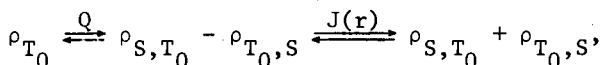
$$s_{\text{conv}} \lesssim Q/3 \quad (3.31a)$$

while for CIDEF one has:

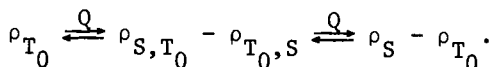
$$s_{\text{conv}} \lesssim Q/80 \quad (3.31b)$$

(where s_{conv} means that the associated P^∞ or F^* is within 10% of its limiting value) e.g., for $Q \sim 10^8 \text{ sec}^{-1}$, P^∞ is generated in about $3 \times 10^{-8} \text{ sec}$ and F^* takes about $0.8 \times 10^{-6} \text{ sec}$ to develop.

This large difference between CIDEF and CIDNP convergence may be understood in terms of the basic re-encounter mechanism. Thus CIDEF involves the two-step path, e.g.,



only the first of which involves Q-mixing and re-encounters. On the other hand, CIDNP involves two successive Q-mixing steps, e.g.,



Thus re-encounters after longer periods of separation are needed for CIDNP. Also, as the polarization effects take longer to develop, other processes such as individual radical T_1 's and T_2 's (ca. 10^{-6} sec) and scavenging reactions, begin to affect the polarization process (cf. [6]). Note that a position and spin-independent "radical-pair"-scavenging reaction can be introduced by adding a term $-k\hat{\rho}$ to eq. 1.27 (or eq. 1.29). This does not affect the diagonalization of \underline{W} . Hence the new eigenvalues become $w_{jj} \rightarrow (w_{jj}-k)$. This is equivalent to letting $s \rightarrow s+k$ in eq. 1.51, so instead of taking the limit $s \rightarrow 0$, one may now take the limit $s \rightarrow k$. But now $\lim_{s \rightarrow 0} \hat{s}p(r_i, s+k) = 0$ for finite k . However, if we

look at the polarization of the radical pairs, as they are scavenged, then we want to collect the polarization contributions expressed as the time integral:

$$P^\infty \equiv \int_0^\infty P_k(t)kdt = kP_k(s=0) = kP(s=k) \tag{3.32}$$

where $P_k(t)$, etc., implies that we have included $-k\hat{\rho}$ in the density matrix equation of motion.

Similarly, we have for F^* :

$$F^* \equiv \int_0^\infty F_k^*(t)kdt = kF_k^*(s=0) = kF^*(s=k) \tag{3.33}$$

Equations 3.32 and 3.33 thus replace eqs. 2.9 and 2.10. When $k \rightarrow 0$ these two approaches become equivalent. But when $k \gtrsim s_{conv}$, the polarization generating mechanism will be interfered with by the rate process. In particular for s (or k) $> 3Q$ one finds that instead of the $(Qd^2/D)^{1/2}$ dependence of P_a^∞ and F^* , one now obtains $P^\infty \propto (Qd^2/D)$ and $F^* \propto (Qd^2/D)^2$. This is due to the fact that the polarization processes are quenched before the reencounter mechanism can be effective, and it is only the effect of the initial encounter which can be observed. The linear and quadratic dependences of P^∞ and F^* on (Qd^2/D) reflect the respective one and two step Q-mixing already noted. The initial encounter mechanism is discussed in more detail in the previous chapters. Note that the logarithmic correction used in eq. 3.11 and Table 1 for F^* may well be reflecting contributions from the initial encounter mechanism as Qd^2/D gets large. See also eq. 3.29 and Table 2 for P_a^∞ , where the role of the initial encounter mechanism is even clearer.

The convergence of the solutions with r_N (for small enough s) may be related to that for s just discussed. Thus, if we use the diffusion expression

$$D = \langle \Delta r^2 \rangle / 6t \approx (2r_N)^2 / 6t \quad (3.24)$$

(where we have assumed that the radical-pair must diffuse apart to r_N and then return for a re-encounter after maximum separation), then we have:

$$r_N/d \approx \left(\frac{3}{2} t_{\text{conv}} D/d^2\right)^{1/2} \approx \left(\frac{3}{2}\right)^{1/2} (D/s_{\text{conv}} d^2)^{1/2} \propto (D/Q)^{1/2} \quad (3.35)$$

Thus, as Q decreases (or D increases), reencounters after longer distances of separation are needed to provide effective Q -mixing and a larger r_N is required.

3.4 Self-consistent method

In the self-consistent method, one sets $K = 0$ in eq. 2.6, and one uses the complete form of $\hat{F}(r)^T$ in eq. 2.7. As a result, the diffusion becomes spin-dependent due to the spin-dependent forces, and the reactivity is explicitly included for $|\hbar J(r)/kT| \gg 1$. The results of such a model have been summarized in [6], and we only touch some of the salient points here. In particular, Fig. 1 corresponds to $U_{SS}(r) \approx -U_{TT}(r) \approx -\hbar J(r)$, $r > d$ and $U_{ST_0}(r) = U_{T_0S}(r) \approx 0$. This results from recognizing that from hydrogen-atom-pair potential surfaces

$$U_{SS}(r) \approx (H_0 + H_1)/(1 + S) \quad (3.36a)$$

$$U_{TT}(r) \approx (H_0 - H_1)/(1 + S) \quad (3.36b)$$

where H_0 is the "Coulomb integral," $H_1 = -\hbar J(r)$ the exchange integral, and S is the overlap integral. Our simplified model is based upon the fact that $H_1 \gg H_0$ for $r > d$ and H_1 is the main source of the attractive forces, while S tends to be small. The strong Coulomb repulsive forces for $r \leq d$ are approximated by a reflecting wall at $r = d$ corresponding to $U_{SS}(r) = U_{TT}(d)$ for $r < d$. It is this model, for which $U_{ST_0}(r) \approx 0$, so that $\rho_{ST_0}(r)$ experiences no net forces, that is approximated by the use of eq. 2.19 as discussed above. [Suppose, however, we were to employ a model for which $U_{SS}(r) = -U(r)$ and $U_{TT}(r) = 0$ for $r > d$, corresponding to an attractive and binding potential for singlets but no potential for triplets (i.e., $H_0 \sim H_1$). Then $U_{ST_0}(r) = -\frac{1}{2}U(r)$, and the resulting self-consistent model would bear a close relation to the phenomenological approach based upon eq. 2.18.]

The main results of the SC model are to demonstrate that

(1) since substantial CIDNP polarizations require non-negligible

values of Λ , and large values $\hbar J_0/kT \gg 1$ are required for reactivity, then the finite range and magnitude of $J(r)$ must be considered in a complete treatment of CIDNP; (2) the effect of the spin-selective reaction of singlets is well approximated by the ASC method (cf. eq. 2.19) in which only the diagonal density matrix elements for singlets react; (3) to a large extent (for RI), the CIDEP polarizations are independent of the details of the spin-selective chemical reaction and they are just linearly dependent on F , i.e., one may just as well use the ASC method as the SC method to calculate P^∞/F (although P^∞ and F are significantly altered); however, (4) since the reaction region is around $r \sim d$, the CIDEP polarization is developed in a region for which $r > d$ such that $\hbar J(r)/kT < 1$.

Note that τ_1 and F^* are easily calculated by eqs. 1.60 and 3.12, respectively, with $U(r) = \hbar J(r)$, and with $\delta = 0$, as expected for very short range interactions. When $\Lambda < 10^{-3}$, then one begins to see CIDEP polarization effects due to the differences in diffusion rates for singlets versus triplets in the polarization region. This leads to a slight excess of singlets generating polarizations. Such effects might possibly be of importance for faster diffusion where non-negligible values of P^∞/F are predicted, but F itself is negligibly small [3].

3.5 Nonspherical radicals

While all current theories are for spherically symmetric exchange interactions, most interacting radicals are expected to display anisotropic features in their exchange interactions and their ability to react. On the basis of our discussion of the SC method it is possible to make some qualitative comments about effects from nonspherical features. First we note that for CIDNP, one expects the primary effect is to lead to a reduction in Λ compared to that predicted for a spherically-symmetric $J(r)$. This is because only that fraction of reencounters for which $\hbar J(\vec{r})/kT > 1$ is important. The effect on CIDEP will, however, be different. It is illustrated in Fig. 2 for a spherical radical (e.g., H atom) interacting with a nonspherical one. Only in Region 1 is $\hbar |J_0|/kT > 1$, as required for a reaction to occur. When a reaction can occur, net triplet character (symbolized by F) is created. Then subsequent reencounters will occur at different regions in Fig. 2 each with its own characteristic range of values of J . Thus while geometric factors will substantially reduce F (via the reduction in Λ), one may still anticipate that P^∞/F (which is independent of F for spherical radicals) need not be very significantly altered. This is because a wide range of J values experienced in reencounters can still lead to comparable polarizations, largely due to the asymptotic dependence of P^∞/F on J_0 (cf. Fig. 2b).

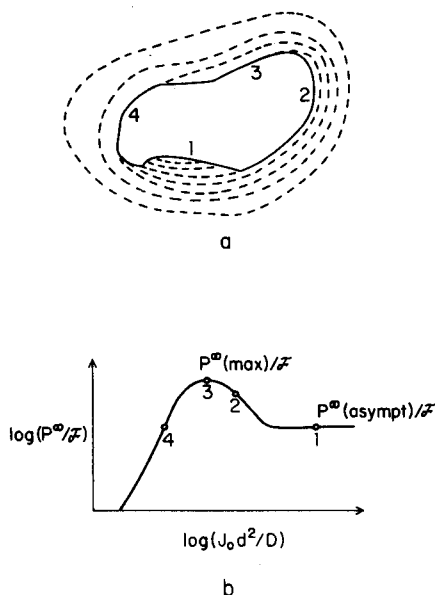


Figure 2. Nonspherical radicals. (a) Suggested contours of constant J value about a nonspherical radical interacting with a spherical radical (e.g., J varies by a factor of 10 between adjacent curves). Spin-selective chemical reaction may occur only at Region 1. (b) Typical variation of P^∞/F with $J_0 d^2/D$ for spherical radicals showing suggested equivalent points corresponding to Regions 1-4 in (a). (By permission from Pedersen and Freed [3].)

4. SPECIAL TOPICS

4.1 Heisenberg spin exchange

We have already discussed the negative role that Heisenberg spin exchange plays in the CIDEP polarization process. It is possible to explicitly calculate the effects of spin depolarization due to Heisenberg spin-exchange. Also, it must be included in a complete treatment of signal intensities [6] (cf. Chapter by Pedersen). Furthermore, such calculations are useful for spin-relaxation studies involving spin exchange [15]. One obtains such results by the finite difference approach by selecting as the initial case: $P_a(t=0) = -1$, or more precisely:

$$2\text{Re}\rho_{S,T_0}(r) = \delta(r-r_I)/r_I^2 \quad (4.1)$$

while $\rho_{SS} = \rho_{TT} = \text{Im}\rho_{S,T_0} = 0$. The calculation then leads to

$$-\Delta P(r_I) = P_a^\infty(r_I, t \rightarrow \infty) - 1 \quad (4.2)$$

where $P_a^\infty(r_I, t \rightarrow \infty)$ is the polarization which remains at the end of the collision, after having started with the initial conditions given by eq. 4.1. Thus $\Delta P(r_I)$ measures the change in polarization at the end of the collision. Typical results have been obtained for the transferred $\Delta P(d_t)$ (cf. eq. 2.22). The results for a contact exchange model [$J(r_j) = J_0 \delta_{r_j, 0}$] bear a simple relation to the well-known analytic result:

$$\Delta P(d_t) \approx \frac{(2J_0 \tau_{1,J})^2}{1 + 4(J_0 + Q^2) \tau_{1,J}^2} [1 - H] \quad (4.3)$$

where $H(Qd^2/D, J_0 d^2/D)$ is a small correction due to the effect of successive reencounters, which tend to generate new polarizations [6] and $\tau_{1,J}$ is given by eq. 3.28a. When one includes the finite range of the exchange, then for small $J_0 < J_0(\max)$ one has a very similar result:

$$\Delta P(d_t) \approx (2J_0 \tau_1(\lambda))^2 [1 - H'] \quad (4.4)$$

with $H' \approx H$ and $\tau_1(\lambda)$ is given by eq. 3.24. However, for $J_0 \gg J_0(\max)$, one finds that $\Delta P(d_t) > 1$, representing the fact that the depolarization can occur for $r > d$. This effect is approximated by:

$$\Delta P(d_t) = g(J_0 d^2/D, \lambda d) \quad \text{for } (|J_0| d^2/D) \gg 1 \quad (4.5)$$

where

$$g(J_0 d^2/D, \lambda d) \approx 1 + (\lambda d)^{-1} \ln[1 + (J_0 d^2/D)(\lambda d)^{-1}] \quad (4.6)$$

The Heisenberg exchange frequency ω_{HE} is then given by [15]:

$$\omega_{HE} = k_2(d') N_p(d_t) \quad (4.7)$$

where we have let

$$k_2(d') \equiv 2\pi D d' \quad (4.8a)$$

(cf. eq. 1.10) and

$$d'/d \equiv g(J_0 d^2/D, \lambda d) \quad (4.8b)$$

while $p(d_t) \equiv \Delta P(d_t)/g(J_0 d^2/D, \lambda d)$. In this notation $k_2(d')$ is the "effective" rate of bimolecular collisions, while $p(d_t)$ (ranging from 0 to 1) is the probability of exchange per collision.

Recently the combined effect of the finite range of $J(r)$ and of ionic effects has been studied [16]. These results may be

summarized by eqs. 4.7, 4.8 and the approximate forms:

$$p(d_t) \approx \frac{(2J_0\tau_1)^2}{1 + (2J_0\tau_1)^2} \left[1 - \frac{h(Qd^2/D)}{1 + 4(J_0^2 + Q^2)\tau_1^2} \right] \quad (4.9)$$

where

$$\tau_1 \approx [d^2/D\lambda d][1 + (\lambda d)^{-1}]f^{*-1}\exp[-U(d)/kT] \quad (4.9a)$$

$$h(Qd^2/D) \sim (Qd^2/D)^{1/2}f^* \quad \text{for } Qd^2/D \lesssim 0.16 \quad (4.9b)$$

and

$$g(J_0d^2/D, \lambda d) \approx \left\{ f^* + (\lambda d)^{-1} \ln \left[\left(\frac{J_0d^2}{D} \right) (\lambda d)^{-1} f^* + 1 \right] \right\} \quad (4.10)$$

The first term in eq. 4.10 is just the usual Debye-Hückel effect on the collision diameter, and the second term approximates the correction due to the finite range of $J(r)$ as well as the Coulombic forces. More detailed results will be given elsewhere [16].

4.2 Spin polarization in two dimensions

The possibility of observing spin polarization in two dimensions is interesting from the point of view of problems in surface catalysis and membrane biophysics. It is no less interesting theoretically, since it affords us a chance to explore the spin polarization mechanism from a different point of view with perhaps new insights. Here we summarize some of the interesting observations one is able to make, in particular from a finite-difference point of view [17]. One can utilize the theory outlined in Sects. 1 and 2 for three dimensions with very little change. The main points are that the diffusion operator given by eqs. 1.2 and 1.3 are first written in cylindrical coordinates; one integrates over the single angle; and one assumes D_z , the diffusion parallel to the principal cylinder axis is zero, so particles remain on the surface. Then the finite-difference solution in two dimensions requires that we now let $\hat{p}(r,t) \equiv p(r,t)$ and the matrix elements of \underline{W} given by eqs. 1.31 now become:

$$W_{j,j\pm 1} = (D/\Delta r^2) [(1 \pm \Delta r/2r_j)] \quad (4.11a)$$

and

$$W_{j,j} = -2D/\Delta r^2 \quad (4.11b)$$

Note, here, that $W_{j+j+1}/W_{j+j-1} = (1+\Delta r/2r_j)/(1-\Delta r/2r_j)$, which says that the rate of transition from larger to smaller values of r is greater than the reverse rate. In three dimensions, one sees by eqs. 1.31, that they are equal. This "inward diffusion" effect, in two dimensions, which is purely geometrical, has a very

important consequence, viz., $t_f(r_I)$ the reencounter probability for initial separation r_I , equals unity independent of r_I . Thus, no matter how far a radical pair confined to an infinite surface is initially separated, if one were to wait a long enough time, then they would ultimately encounter (provided only they are not scavenged or destroyed in some other manner). This has to have important consequences in the spin polarization process, since it means that the radical-pair "collision" is never complete as $t \rightarrow \infty$, unless other processes, such as radical scavenging, radical T_1 , or radicals leaving the surface succeed in terminating the process.

We have presented a preliminary summary in ref. [18] of S-T₀ results for finite r_N but as $t \rightarrow \infty$. The effect of an outer collecting wall at r_N is to terminate the process, but our results show they tend toward their limiting values for $r_N \rightarrow \infty$ as a function of $\ln(r_N/d)$. Here we summarize some of our S-T₀ results [18] from the other point of view of large r_N but finite t , or more precisely finite $s > 0$. In order to do so, it is useful to define a quantity L given by:

$$L(s,c) \equiv \ln[1 + c(D/sd^2)^{\frac{1}{2}}] \quad (4.12)$$

so $\lim_{s \rightarrow 0} L(s,c) \rightarrow \infty$. Then for $L(s,2) > \ln(r_I/d)$ one has:

$$t_f(r_I) \approx 1 - \frac{\ln(r_I/d)}{1 + L(s,2)} \quad (4.13)$$

which approaches unity as $s \rightarrow 0$. Similarly, one has for $\Lambda(s)$:

$$\Lambda(s) \approx \frac{k\tau_1 L(s, 4/3)}{1 + k\tau_1 L(s, 4/3)} \quad (4.14)$$

so the reactivity also approaches unity as $s \rightarrow 0$. This makes sense, since for finite $k > 0$, the radical-pair will continue to reencounter until they finally react. We may therefore think of τ_1 , the effective duration of the collision as becoming $\tau_1 L(s, 4/3)$. Now, for CIDNP:

$$F^*(s) \approx \frac{(Q/2s)^2}{1 + (Q/2s)^2 (Qd^2/D)^{-0.2} [L(s, 2^{-1/2})]^{-1} [1 + (Qd^2/D)^{0.2} L(s, 2^{-1/2})]} \quad (4.15)$$

which for small sd^2/D becomes:

$$F^* \approx \frac{L(s, 2^{-1/2}) (Qd^2/D)^{0.2}}{1 + L(s, 2^{-1/2}) (Qd^2/D)^{0.2}} \quad (4.16)$$

which increases as $s \rightarrow 0$ to its maximum value of unity. Equation 4.15, in its essentially quadratic dependence upon Q , is thus very different than the Q^2 behavior of eq. 2.32 which is appropriate for three dimensions. In fact, it is more nearly the behavior associated with an "initial encounter" mechanism (cf. discussion below eq. 3.33). On this basis, one might venture to suggest that in two dimensions, the role of the initial encounter, in which Q mixing occurs during the encounter, is the dominant process. The role of the reencounter is then essentially just to begin anew the "initial encounter" process.

Why is there such a change from the three-dimensional mechanism? It appears likely that this is due to the "inward diffusion" effect in two dimensions (cf. discussion of eqs. 4.11), which will tend to keep the radical-pair closer together for longer periods of time. Nevertheless, it is interesting to note that all of the model-independent, exact relations eqs. 2.24-2.29 still hold true.

We see a very similar effect in the results for CIDEP. Thus for contact exchange [and $(4/7)(D/sd^2)^{1/2} > 1$], one has:

$$P_a(s) \approx \frac{\frac{5}{6}(Q/s)}{1 + b(Q/s)(Qd^2/D)^\epsilon} \left[\frac{2J_0\tau_{1,J}}{1 + \frac{13}{4}(2J_0\tau_{1,J})^2 L(s, \frac{4}{7})} \right] \quad (4.17)$$

with $b = 5/2$ and $\epsilon = 0.2$ for $(2J_0\tau_{1,J})^2(13/4)L(s, 4/7) \ll 1$ and $b = 3/4$ and $\epsilon = -0.15$ for $(2J_0\tau_{1,J})^2(13/4)L(s, 4/7) \geq 1$. Equation 4.17 shows a linear dependence on Q , which is again just what is expected for the "initial encounter" mechanism. When we introduce a finite λ , then the results are approximated by:

$$P_a(s) \approx \frac{(8/7)(Q/s)}{1 + \frac{8}{3}(Q/s)(Qd^2/D)^{0.25}} 2J_0\tau_1(\lambda) \quad (4.18a)$$

for $(2J_0\tau_1(\lambda))^2 \frac{8}{3} L(s, \frac{4}{7}) \ll 1$

with

$$\tau_1(\lambda) \approx \frac{7}{8} \frac{d}{\lambda D} \left[1 + \frac{1}{2} \frac{1}{\lambda d} \right] \quad (4.18b)$$

and by:

$$P_a(s) \approx \frac{\frac{3}{5}(D/20sd^2)^{3/2}(Qd^2/D)[2J_0\tau_1(\lambda)]^{-0.02}}{1 + \frac{13}{2}[L(s, \frac{4}{7})]^{2.75}(D/20sd^2)^{3/2}(Qd^2/D)^{0.85}(d^2/\tau_1(\lambda)D)^{1/2}} \quad (4.19)$$

for $(2J_0\tau_1(\lambda))^2 \frac{8}{3} L(s, \frac{4}{7}) > 1$.

On the other hand, the results for Heisenberg spin exchange do not suggest a fundamental change in mechanism, except for the

fact that $t_f = 1$. Thus for contact exchange one has:

$$\Delta P(s, d_t) \approx \frac{[L(s, \frac{3}{10})]^2 (2J_0 \tau_1)^2}{1 + [L(s, \frac{3}{10})]^2 4(J_0^2 + Q^2) \tau_1^2} [1 - f] \quad (4.20)$$

where $f(Qd^2/D) \approx (Qd^2/D)^{1/2}$ for $Qd^2/D < 1$, and $f(Qd^2/D) = 1$ for $Qd^2/D \geq 1.6$. One can recover the three-dimensional result of eq. 4.3 merely by letting $L(s, 3/10) \rightarrow 1$ in eq. 4.20 [except for $f(Qd^2/D)$].

Again, for finite λ we have:

$$\Delta P(s, d_t) \approx [L(s, \frac{15}{8})]^2 (2J_0 \tau_1(\lambda))^2 [1-f]$$

for $(2J_0 \tau_1(\lambda))^2 [L(s, \frac{15}{8})]^2 \ll 1$ (4.21)

and

$$P(s, d_t) \sim 1 + \frac{\ln(1 + J_0 d^2/D)}{\frac{\lambda d}{\sqrt{3}} [L(s, \frac{15}{8})]^2} \text{ for } (2J_0 \tau_1(\lambda))^2 L(s, \frac{15}{8})^2 \geq 1 \quad (4.22)$$

The above results can be approximately related to solutions summarized in [18] for Λ , F^* , and P_a as a function of r_N/d by letting

$$s^{-1} \rightarrow [(r_N)^2/4D] [\ln(r_N/d) - \frac{1}{2}] \quad (4.23)$$

Another very interesting feature of the two-dimensional theory compared to three dimensions is the fact that the convergence conditions on r_M , and r_N are significantly altered. These changes occur because of the $(1 \pm \Delta r/2r_j)$ factor in eq. 4.11 for $W_{j,j+1}$, and because of the new role of the reencounter process. One finds that the "inward diffusion" effect is considerably amplified by introducing the factor $f \gg 1$ at r_M (cf. eqs. 1.40), and this interferes with the convergence of the solutions. That is, in $\vec{\rho}$ space, one is introducing an additional reflected "wave" component at r_M . Such an effect is found to be unimportant in three dimensions but of considerable importance in two dimensions. Thus, it was deemed desirable to avoid altogether any change in the finite-difference element (i.e., let $f = 1$). This means that it is not conveniently possible to use values of $r_N/d \sim 10^3$ as was found necessary for convergence in three dimensions. However, because of the changed role of the reencounter mechanism in two dimensions, and the relatively simple asymptotic dependence on $\ln(r_N/d)$ [17,18], it becomes only necessary to use values of r_N/d such that the inequality

$$(r_N/d)^2 [\ln(r_N/d) - \frac{1}{2}] > 4D/d^2 s \sim 4Dt/d^2 \quad (4.24)$$

(cf. eq. 4.23) is obeyed; i.e., r_N is large enough to converge to

the correct solution for finite t (or s). Once this is satisfied, the solution is obtained as a function of s anyway! In this manner, satisfactorily convergent solutions are obtained for $r_N \lesssim 25$.

The use of these quantities $\Lambda(s)$, $F^*(s)$, $P_a(s)$, and $\Delta P(d_t, s)$ in the time-evolution expressions of actual observables (cf. [6] and Pedersen's chapter for three dimensions), will be given elsewhere [17]. However, we may simply note here that if k represents a first order rate constant for interrupting the process (e.g., rate of desorption from a surface), then one is interested in values for $s \sim k$.

Finally we note these two-dimensional results are a good example of how, by a combination of approximate fits of the numerical results to relatively simple analytical forms, one is able to obtain a great deal of insight into what is physically a very different result than in three dimensions.

4.3 Low-field spin polarization

Low-field spin polarization is discussed in Adrian's chapter. One finds that only CIDNP effects are important, while CIDEP effects are too small to be of interest. From our point of view, in low fields it is necessary to include the $\rho_{T_{\pm}T_{\pm}}$ terms in eq. 2.11 to determine the CIDNP effects. This is because of the significant role played by S - $T_{\pm 1}$ mixing by the hyperfine interactions. That is, suppose one of the interacting radicals has no nuclear spins, while the other has a nuclear spin I . We class the combined electronic and nuclear spin states by $|i, M_I\rangle$ where $i = S, T_0$, or T_{\pm} , while M_I is the nuclear-spin quantum number. Then we can write for the Hamiltonian $H(r)$ [cf. eq. 2.13] in this basis:

$ S, M_I\rangle$	$ T_0, M_I\rangle$	$ T_+, M_I-1\rangle$	$ T_-, M_I+1\rangle$	
$2J(r)$	A	-B	B ⁺	
A	0	B ⁻	B ⁺	
B ⁻	B ⁻	C ⁻	0	
B ⁺	B ⁺	0	-C ⁺	(4.25)

where:

$$A \equiv \frac{1}{2} (g_a - g_b) \beta_e \hbar^{-1} B_0 + \frac{1}{2} A M_I \quad (4.26a)$$

$$B^{\pm} \equiv \frac{1}{\sqrt{8}} A [I(I+1) - M_I(M_I \pm 1)]^{\frac{1}{2}} \quad (4.26b)$$

$$C^{\pm} = \frac{1}{2} (g_a + g_b) \beta_e \hbar^{-1} B_0 + \frac{1}{2} A (M_I \pm 1) \quad (4.26c)$$

Thus, in low fields, one now has a 16×16 matrix representation of H^x for each value of r (i.e., $\underline{\Omega}$ is still block diagonal, but each block is 16×16). However, this leads to matrices of huge size to be solved. Thus, for typical high-field solutions one has $r_N \sim 5 \times 10^3 \text{ \AA}$, or $N \sim 300$ (with $M \sim 100$, $\Delta r = \frac{1}{4} \text{ \AA}$ and $f \sim 100$). In low field, the complete super matrix will be of order $16 \times 300 = 4,800$ with a bandwidth of 33. Thus considering just the banded portion of such a matrix, one needs to store $\sim 160 \text{ K}$ elements as double precision complex numbers (16 bytes/matrix element). This means that the matrix storage alone requires about 2.4 Megabytes of core, in order to employ a standard matrix inversion routine, such as DGELB (cf. Table A #4), which is otherwise a very reliable method. Because of such enormous core requirements, we have been examining other computer algorithms which would permit the extensive use of storage devices, because at a given step in the solution they need only operate on a portion of the complete super-matrix [19]. Simpler Gaussian elimination methods (cf. Table A #5) can be used in such a manner. But, without employing Gaussian elimination with complete pivoting as does DGELB, one encounters difficulties, because the CIDNP super-matrices are ill-conditioned. For our purposes, this means that for small s , the off-diagonal elements of $\underline{\Omega}$ are not small compared to the diagonal elements.

Diagonalization methods, which do not require complete matrix storage in core, and which are not subject to the ill-conditioned problem, may well be the most fruitful, (e.g., Table A #2). Other approaches are based on a direct study of time-dependent solutions as opposed to solutions in Laplace space (cf. below).

4.4 Time-dependent solutions

We have already noted that the stochastic-Liouville equation in the form of eq. 2.8 could be solved by standard matrix diagonalization procedures operating on $A = \underline{W}' - \underline{K}' + i\underline{\Omega}$ (cf. Table A #1) by analogy to the method outlined by eqs. 1.50-1.53 for diagonalizing \underline{W}' as employed in [11]. This would yield time-dependent solutions when desired (cf. eq. 1.52). Such methods would require the storage in core of A as well as the complex orthogonal matrix \underline{Q} (provided $\underline{W}' - \underline{K}'$ has been previously symmetrized by a matrix like \underline{S} of eq. 1.48).

For problems involving very large matrices (e.g., low-field CIDNP), one may propose an alternative procedure [19]. First, one may explicitly solve the finite difference equations in t space [20]. That is, one solves eq. 2.1 (cf. eq. 2.8) as:

$$\hat{\rho}(t) = [-i\underline{\Omega} + \underline{W}' + \underline{K}'] \Delta t \hat{\rho}(t - \Delta t) + \hat{\rho}(t - \Delta t) \quad (4.27)$$

Actually, it is found [19] that eq. 4.27 does not lead to a stable

finite difference method, because it does not exactly preserve conservation of probability (for $\underline{K}' = 0$). This problem can be resolved as follows. We first rewrite eq. 4.27 in a manner that is correct to lowest order in Δt (as is eq. 4.27 itself). That is

$$\hat{\underline{\rho}}(t) \approx (\Delta t \underline{W}' + \underline{1}) (\underline{1} - i \underline{\Omega} \Delta t + \underline{K}' \Delta t) \hat{\underline{\rho}}(t - \Delta t) \quad (4.28a)$$

Then:

$$\hat{\underline{\rho}}(t) \approx (\Delta t \underline{W}' + \underline{1}) [\exp(-i \underline{\Omega} \Delta t + \underline{K}' \Delta t)] \hat{\underline{\rho}}(t - \Delta t) \quad (4.28b)$$

Equation 4.28b is the basis of an effective finite difference method [19]. One then solves $\hat{\underline{\rho}}$ for each time t in terms of the previously obtained solution at the previous time $t - \Delta t$. The stability condition on \underline{W}' for such a method is

$$\frac{2\Delta t}{(\Delta r)^2} D \leq 1 \quad (4.29)$$

so that the diagonal elements of $\underline{W}' \Delta t$ are smaller than unity. (A convenient value of $\Delta t \sim 10^{-12}$ sec for $D \sim 10^{-5}$ cm²/sec, $\Delta r \sim \frac{1}{4}$ Å). However, such a method still requires that \underline{A} be stored in core. We can improve on this by taking further advantage of the separation of the solution into the two parts relating to $\underline{K}' - i \underline{\Omega}$ and \underline{W}' , and recognizing that if \underline{W}' is spin-independent, then we can separately diagonalize each $L^2 \times L^2$ block of $\underline{K}' - i \underline{\Omega}$ as needed. Now the \underline{W}' matrix has simple elements (cf. eqs. 1.31). Thus, eq. 4.28b is easily solved for each value of r_i utilizing only a small portion of the total $L^2 \times N$ dimensional space [19]. The ensuing iterative process can efficiently employ an external storage device with a minimum core requirement (cf. Table A #3).

In this way, one can contemplate newer computer algorithms to solve more challenging CIDNP/CIDEP problems.

4.5 The triplet mechanism for CIDEP

This topic is discussed in the chapter by Atkins from the point of view of analytical or perturbation methods. The main point to be made here is that the triplet mechanism involves rotational diffusion which modulates the zero-field triplet tensor. Thus an analytical solution of the density matrix analogous to eqs. 1.17-1.19 given for translational diffusion is appropriate. The eigenfunctions for rotational diffusion are the generalized spherical harmonics. Such a point of view was utilized by Pedersen and Freed [6,10]. When, however, the tumbling motion slows down sufficiently and/or the zero-field splitting increases, then the lowest order perturbation approach breaks down, and one must use a numerical approach analogous to eqs. 1.21 and 1.22 to solve for the coupled algebraic equations resulting from the eigenfunction

expansions in generalized spherical harmonics. A comparison of these numerical solutions has shown that perturbation-type approaches are adequate for

$$D^2 \lesssim \frac{1}{2} [\omega_0^2 + \tau_R^{-2}] \quad (4.30)$$

where D is the zero-field splitting constant, ω_0 is the ESR Larmor frequency, and τ_R is the rotational correlation time. When this inequality is not satisfied, then the numerical solutions are required. They are discussed further in [6] and [10].

ACKNOWLEDGMENT

I wish to thank Mr. Gary P. Zientara for his extensive help in preparing these lectures.

REFERENCES

1. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 57, 1004 (1972).
2. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 58, 2746 (1973).
3. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 59, 2869 (1973).
4. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 61, 1517 (1974).
5. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 62, 1790 (1975).
6. J.H. Freed and J.B. Pedersen, *Adv. Mag. Res.* 8, 1 (1976).
7. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Oxford Univ. Press, London and New York, 1959, p. 382.
8. F.C. Collins and G.E. Kimball, *J. Colloid Sci.* 28, 425 (1949).
9. B. Yoon, J.M. Deutch, and J.H. Freed, *J. Chem. Phys.* 62, 4687 (1975).
10. J.B. Pedersen and J.H. Freed, *J. Chem. Phys.* 62, 1706 (1975).
11. L.P. Hwang and J.H. Freed, *J. Chem. Phys.* 63, 4017 (1975).
12. J.B. Pedersen, in *Electron-Spin Relaxation in Liquids* (L.T. Muns and P.W. Atkins eds.), Ch. III, Plenum, New York, 1972.
13. L.P. Hwang and J.H. Freed, *J. Chem. Phys.* 63, 118 (1975).
14. U. Fano, *Rev. Mod. Phys.* 29, 74 (1957).
15. M.P. Eastman, R.G. Kooser, M.R. Das, and J.H. Freed, *J. Chem. Phys.* 51, 2690 (1969).
16. S.A. Goldman, J.B. Pedersen, and J.H. Freed (to be published).
17. G.P. Zientara and J.H. Freed (to be published).
18. J.H. Freed, *ACS Symp. Issue* 34, Ch. 1 (1976).
19. G.P. Zientara and J.H. Freed (unpublished).
20. Z. Schulten and K. Schulten, *J. Chem. Phys.* (in press).

Appendix: Table A. Typical Numerical Methods in the Solution of CIDNP/CIDEP Problems^a

General Method	Equation Solved ^b	Specific Method	Typical Numerical Algorithm(s) ^d
(1) Matrix Diagonalization (for time dependent solutions)	Solve for $\underline{a}_d = \underline{T} \underline{A} \underline{T}^{-1}$ where \underline{a}_d is diagonal	(1) Diagonalization of the entire matrix	Complex Jacobi Rotations
(2)		(2) Diagonalization with use of storage devices	Complex Rotations via a modified Givens method
(3)		(3) Analytic diagonalization (each r-value) with iterative diffusive steps	Explicit forward difference or Crank-Nicolson schemes
(4) Direct Solution via matrix inversion (solution in Laplace space)	Solve $\hat{\underline{p}}(\underline{r}, s) = (\underline{s} \underline{I} - \underline{A})^{-1} \hat{\underline{p}}_0(\underline{r})$	(4) Inversion of the entire matrix	Gaussian elimination with complete pivoting
(5)		(5) Inversion via locally active algorithms	Simple Gaussian elimination in combination with other techniques
(6) Direct Solution via iterative matrix inversion	Solve equation as for (4) and (5) iteratively ^c	(6) Inversion row by row by successive approximations	Gauss-Seidel or Successive Over-relaxation iterative methods

Table A (continued)

Major Mathematical Constraint(s)	Major Computing Requirements	Core Requirements ^f	External Storage Permitted	Useful for Mini-Computer	Status ⁱ
(1) None	\underline{A} (banded), \underline{T} (full) must fit in core	$(2L^2+1)(N \times L^2) + (N \times L^2)$	No	No	WM
(2) None	Sophisticated use of storage devices	Minimal-approx. $2(2L^2+1)$	Yes	Yes	WIP
(3) Eq. 4.29	Minimal core requirements, and as (2)	Minimal-approx. $3(L^2 \times L^2)$	Yes	Yes	WIP
(4) $(\underline{s}\underline{L} - \underline{A})$ must be nonsingular (as it is for $s \neq 0$)	\underline{A} (banded) must fit in core	$(2L^2+1)(N \times L^2)$	No	No ^g	WM ^j
(5) $(\underline{s}\underline{L} - \underline{A})$ must be diagonally dominant	Solution collapses if mathematical condition not satisfied due to round-off errors	Approx. $(2L^2+1)(L^2 \times 20)$	No	Yes ^h	WIP
(6) Same as for (5) ^e	Solution will not converge if mathematical condition not satisfied	Minimal-approx. $(2L^2+1)$	Yes	Yes	No future utility seen in CIDNP/CIDEP

Table A (continued)

Speed of Solution	Utility	References
(1) Fastest time resolved (TR) method	Small N, high field for TR studies	<u>Gordon and Messenger in Muus' Electron Spin Relaxation in Liquids</u> , Plenum, New York (1972), Ch. 13.
(2) Moderate TR method	Low field, large N for TR studies (large matrices)	<u>Numerical Analysis of Symmetric Matrices</u> , by H. Schwarz, Prentice-Hall, Englewood Cliffs, N.J. (1973); and <u>Mathematical Methods for Digital Computers</u> , by Ralston and Wilf, Wiley, New York (1960), Vols. I, II; among others.
(3) Slowest TR method	Low field, moderate N for TR studies (large matrices)	<u>Difference Methods for Initial Value Problems</u> , by Richtmyer and Morton, Wiley-Interscience, New York (1967), pp. 17, 189.
(4) Fastest method (for given s value)	High field in 2 and 3 dimensions	Subroutine DGELB, from the IBM Scientific Subroutine Package.
(5) Moderate V.E.	Low field, large N not feasible for 3D s → 0 limit	Same as (2).
(6) Very slow	Unfavorable as CIDNP/CIDEP matrices do not suit mathematical requirements	<u>Matrix Iterative Analysis</u> , R. Varga, Prentice-Hall, Englewood Cliffs, N.J. (1962), p. 58.

Footnotes to Table A

a) Table prepared by G.P. Zientara.

b) $\underline{A} = \{\underline{W}' - i\underline{\Omega} - \underline{K}'\}$.

c) If we let $\underline{A} = (\underline{L} + \underline{D} + \underline{U})$ where \underline{L} , \underline{D} , \underline{U} are matrices composed of the elements of \underline{A} below the diagonal, the diagonal elements, and the elements above the diagonal respectively. Using the Gauss-Seidel method one would solve for the k th approximation to $\hat{p}(r,s)$ from:

$$\underline{p}^{(k)}(r,s) = (s\underline{I} - \underline{D})^{-1} [\hat{p}_0 + (\underline{L} + \underline{U})\underline{p}^{(k-1)}(r,s)].$$

d) Many more algorithms (some favorable, some not) exist than are mentioned here.

e) By diagonally dominant is meant,

$$(s - \Lambda_{ii}) > \sum_{\text{all } j \neq i} |\Lambda_{ij}| \text{ for all } i.$$

This condition suffices for our problems as more rigorous mathematical treatments lead to similar conditions [cf. James and Riha, SIAM J. Numer. Anal. 12, 137 (1975)].

f) Given as the number of matrix elements needed in core for solution (1 matrix element = 16 bytes). This is based on an LxL Hamiltonian matrix and N locations used in finite difference r-space.

g) If this is implemented with a computer algorithm utilizing storage devices, it is extremely time consuming and therefore unfavorable.

h) For CIDNP/CIDEP in the contact exchange cases only.

i) WM = working method, WIP = work in progress on the numerical method.

j) The method used by Pedersen and Freed in their studies.