A unified approach to spin polarization (CIDEP) and relaxation by Heisenberg spin exchange. I. Generalized equations for reactive radicals

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A theory of Heisenberg spin exchange (HSE) has been formulated in this and the following paper to consider the processes of chemically induced dynamic electron polarization (CIDEP) and relaxation. The framework, which includes all the spin states of a radical pair (RP), relies on an exact transient solution of the encounter RP density matrix. To aid in interpreting time-resolved ESR studies of these effects, a nonphenomenological formulation of Bloch-type equations is explicitly derived for the $\cdot$RH and $\cdot RH_2$ radical spin systems as well as for general radical systems in terms of their n-line ESR spectra. The longitudinal and transverse relaxation rates and the frequency shifts are calculated for conditions spanning the weak to the strong exchange limit under a wide range of viscosities. The normally slight frequency shifts are shown to be strongly enhanced by CIDEP although not to an extent that is easily observable. Aside from the usual degeneracy effects, a curious HSE relaxation behavior is predicted for ESR lines that exhibit multiplet CIDEP, wherein the observed longitudinal relaxation rate can appear faster than the transverse rate by an amount that depends on the degeneracy of the line vs the total number of transitions of the radical. The present theory is formulated to be descriptive of time-resolved ESR experiments. Implications to reactive radicals are discussed and the solutions of the modified Bloch equations are presented to consider (i) instantaneous, geminate, and diffusive RP CIDEP, (ii) coupled and time dependent relaxation by HSE, and (iii) second-order chemical decay.

I. INTRODUCTION

Recent advances in time-resolved (TR) ESR has led to considerable activity in the areas of CIDEP and relaxation,[1-7] which in turn has given us new detailed dynamical information on radical–radical interactions in solution. Frequency-resolved studies on transient radicals exhibiting CIDEP have proven invaluable for radical identification and structural elucidation in the course of a chemical reaction. Its importance has also been demonstrated for gaining insight into properties affecting polarization and relaxation. Time-resolved studies have provided detailed probes of processes immediately following radical collisions. Accurate measurements of polarization production and relaxation processes have shed light on the short range interactions between radicals. The TR ESR methods that have emerged to address the above areas of interest are the cw method (modified for improved time resolution)[1-3] and the pulsed method (FID[4] or spin echo[5-7]). Both methods have their adherents, however the basic benefits to cw ESR (greater sensitivity) and pulsed ESR (greater time resolution) make them complementary and not competing techniques.

It has been recognized for some time that the exchange interaction J between the electron spins of free radicals can give rise to the disparate processes of relaxation and polarization (CIDEP). The correspondence between these effects, however, has not been widely appreciated since they arise in rather different ways. Relaxation can occur for *any* radical pair (RP) encounter and is greatest for strong interaction ($J\tau_e \gg 1$, where τ_e is an effective encounter duration).[8-12] CIDEP, on the other hand, requires phase correlated encounters of *previously paired* radicals and is most efficient for weak to intermediate exchange strengths ($J\tau_e \simeq 1$).[8,13] Vector models have been developed which help to visualize these effects.[8] The strength of the exchange interaction J is a function of the interradical distance r. Hence, the diffusion and impact parameters for RP encounters play an important role. Since a large distribution of J values is possible, both polarization and relaxation can occur in the same system. Despite the correspondence between these two processes by the exchange interaction, little progress has been made toward unifying relaxation and polarization under one theory.[14]

The first theories of Heisenberg spin exchange (HSE) considered only T_2 measurements from cw ESR experiments[9] and hence were derived in terms of line shape functions using steady state solutions.[9-11] Extensions to saturation recovery and ELDOR experiments soon followed in order to describe T_1 measurements.[12] Since these theories were modeled for unreactive radicals, they resembled approaches taken to describe chemical exchange effects in NMR.[15] Theories on the radical pair mechanism (RPM) of CIDEP exist at many levels of rigor.[13,16-18] However, in virtually all instances, the high field limit is employed so as to reduce the problem to just two RP electron spin states (i.e., S and T_0). Relaxation effects have been treated within this basis and are referred to as polarization quenching.[17] However, the S and T_0 basis ignores the $\alpha\alpha$ and $\beta\beta$ RP states which are critical to a complete description of relaxation by HSE.

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Since CIDEP and relaxation by spin exchange are best formulated using different electron spin basis sets, the two processes have invariably been treated separately. In a previous paper,[14] we outlined a procedure for unifying the RP mechanism of CIDEP and relaxation under a single framework for HSE by considering all the spin states of the RP. The intent of this and the following paper[19] is to develop the formalism more thoroughly by generalizing it for all exchange strengths and for any size radical spin system.

In paper I, we begin with a conventional method for modeling exchange-type processes, however, we carry out an exact (transient) solution of the encounter pair density matrix. In the past, the solution to this problem has relied on either (i) steady state solutions,[11] (ii) strong exchange limits, or (iii) permutation operators (which implicitly assumes strong exchange).[10,20] These methods are fine for describing relaxation, since this process is most effective for strong exchange, however, they fail to uncover the transient terms which account for CIDEP. Here, we demonstrate that the encounter RP density matrix can be solved exactly by invoking very realistic assumptions. The solution is independent of experimental technique and, therefore, appropriate for any detection method. The solution is then incorporated into the density matrix equations for the free radical. These equations have also been formulated in terms of nonphenomenological Bloch-type equations so as to be of assistance in analyzing TR ESR studies of reactive radicals. They are particularly relevant to recent studies that measure both intrinsic CIDEP enhancements and relaxation rates by HSE.[4,5,21] Previous sets of Bloch equations adapted for CIDEP studies have relied on phenomenological CIDEP terms and other approximations and were not capable of accounting for the dependence of relaxation rates on the exchange strength.[5,22–24]

Hore and McLauchlan have recently derived a set of Bloch equations to consider spin exchange in radicals.[22] They adopted the method of McConnell[20] of permutating spins to model the exchange (thus assuming the strong exchange limit) and employed phenomenological descriptions of CIDEP and relaxation. This construction has been shown to work successfully for a number of radical systems that develop triplet mechanism (TM) CIDEP.[2,22] In the present formalism, we have removed the restrictions of the strong exchange limit on HSE relaxation by describing the RP encounter interactions via a generalized density matrix solution. The RP mechanism of CIDEP falls naturally out of this treatment thereby bridging the correspondence between relaxation and polarization via HSE for the first time. The importance of the present derivation is that it is nonphenomenological and completely general for all exchange strengths.

In paper II,[19] we extend the theory to consider a model for the interradical distance dependence of $J(r)$ which leads to simple analytic expressions for the CIDEP enhancement factor E and the exchange frequency ν_{ex}. Existing theories of RPM CIDEP which consider the $J(r)$ dependence in calculating E involve tedious computations or numerical solutions.[8(b),17,18] Finally, we relate E and ν_{ex} to other experimentally measurable quantities to provide a more detailed understanding of RP dynamics. Extensive comparison with experimental work as well as analyses based on other theories of CIDEP are made.

The outline of paper I is as follows. In Sec. II, we describe the general procedure for solving the RP density matrix and develop the nonphenomenological Bloch equations for the free radicals. In Sec. III, we evaluate the modified Bloch equations for specific spin systems. For the ·RH spin system (Sec. III A), the effects of high viscosity and weak exchange are examined in detail. The $\cdot RH_2$ (Sec. III B) and the general n spin-$\frac{1}{2}$ case (Sec. III C) are also treated including chemical decay and concentration dependent effects. In Sec. IV, applications of the modified Bloch equations to TR ESR experiments are described. Implications to reactive radicals are discussed (Sec. IV A) and solutions of the Bloch-type equations are given (Sec. IV B). Finally, the summary and conclusion of this work is presented in Sec. V.

II. THEORY

A. General equations

We begin by employing a traditional density matrix approach for two spin systems that undergo exchange-type processes[25] given by

$$\dot{\rho} = \dot{\rho}_{\text{exch}} + i[\rho, H] + R\rho, \tag{2.1}$$

where

$$\dot{\rho}^a_{\text{exch}} = [\langle \text{Tr}^b \rho_e \rangle - \rho^a]/\tau_f, \tag{2.2}$$

where ρ and ρ_e are the density matrices of the free radical and the encounter radical pair, respectively, and τ_f is the mean time between free radical encounters. The term $R\rho$ is included to account for spin-dependent chemical decay and for relaxation from processes other than spin exchange. In Eq. (2.2), and henceforth, we focus on a single radical (i.e., a) of the radical pair: Hence, the trace operation sums over the states of the partner radical (i.e., b) not under consideration. One could likewise symmetrize the trace operation over both radicals (in the case of identical radicals),[14] however, the result would be the same.

The equation of motion for ρ_e is given by

$$\dot{\rho}_e = i[\rho_e, H_e] \tag{2.3}$$

which is solved exactly over the duration of an encounter. The solution, following the trace operation in Eq. (2.2), is then averaged over a distribution of encounter times. We assume as in previous treatments[26] that the translational correlation function for radical pair separation is exponential and average according to the relation

$$\langle \rho_e \rangle = \frac{1}{\tau_e} \int_0^\infty \rho_e(t) e^{-t/\tau_e} dt, \tag{2.4}$$

where τ_e is the mean time between diffusive steps and which, therefore, can be associated with the mean duration of an encounter. If the common condition $\tau_f \gg \tau_e$ holds, then the free radicals and not the radical pairs will be the observables. The free radical (FR) and radical pair (RP) Hamiltonians in a magnetic field are given, respectively, by

$$H^a = (\omega_0 - \omega) S^a_z - (\omega_n + \omega) \times \sum_i^a I_{zi} + \sum_i^a a_i \mathbf{I}_i \cdot \mathbf{S}^a + \omega_1 S_x, \tag{2.5}$$

$$H_e = H^a + H^b + J(r)\mathbf{S}^a\cdot\mathbf{S}^b, \tag{2.6}$$

where $\frac{1}{2}J(r)$ is the negative of the exchange integral, ω_0 is the Larmor frequency (i.e., $g\mu H_0$, where the symbols have their usual meaning), ω is the rotating frame frequency, and a_i are the hyperfine splittings. We express the nuclear spin frequencies by a single ω_n term since the differences in frequencies due to chemical shifts, spin–spin splittings, or different nuclei are insignificant in the frequency range of consequence [e.g., a_i, ω_0, $J(r)$]. We have included a microwave excitation field, denoted by the nutation frequency ω_1, for the free radicals. We assume that the interaction is negligible over the duration of a RP encounter (i.e., $\omega_1 \ll \tau_e^{-1}$).

The functional form of $J(r)$ is model independent. We therefore denote $J(r)$ simply as J, although the RP distance dependence is inferred. In paper II,[19] we present a specific model for treating the distance dependence of $J(r)$.

B. Modified Bloch equations

Here we show that the density matrix equations may be cast in the form of modified Bloch equations. This is done as a convenience to those accustomed to using modified Bloch equations in analyzing TR ESR results. Although some similarities with existing phenomenological equation[5,22–24] will naturally be evident, we emphasize that the present Bloch-type formulation for CIDEP and relaxation by HSE is *not* phenomenological, but rather is derived from an exact density matrix solution.

The transformation of the density matrix to Bloch equations is accomplished by the trace relation $M = \mathrm{Tr}\{\hat{S}\rho\}$, where M is the electron spin magnetization which is related to a component $\hat{S}$ of the total angular momentum operator $\mathbf{S}$. This gives for the transitions between states $|k\rangle$ and $|l\rangle$ corresponding to the observable ESR signals of the free radicals, the relations

$$\dot{M}_{+,kl} = \dot{\rho}_{lk}, \tag{2.7a}$$

$$\dot{M}_{-,kl} = \dot{\rho}_{kl} = \dot{\rho}^*_{lk}, \tag{2.7b}$$

$$\dot{M}_{z,kl} = \tfrac{1}{2}(\dot{\rho}_{kk} - \dot{\rho}_{ll}). \tag{2.7c}$$

The elements of ρ for the free radical are described by

$$\dot{\rho}^a_{kl} = \tau_f^{-1}\left[\left\langle\sum_\mu \rho_{k\mu,l\mu}\right\rangle - \rho^a_{kl}\right] + i\sum_m [\rho^a_{km}H_{ml} - H_{km}\rho^a_{ml}] - \left[\frac{\rho_{kl}-\rho^0_{kl}}{T_{10}}\right]_{k=l} - \left[\frac{\rho_{kl}}{T_{20}}\right]_{k\neq l} - \frac{\rho_{kl}}{T_{R,kl}(t)}. \tag{2.8}$$

We have shown that phenomenological terms for uncoupled relaxation, T_{10}^{-1} and T_{20}^{-1}, and spin-dependent reaction probabilities T_R^{-1} may be added to the density matrix equations if desired. However, we mention that they are independent of the HSE terms which are solved exactly. We drop the phenomenological terms until we arrive at the generalized modified Bloch equations (Sec. III C).

The differential equations for the encounter RP are given by

$$\dot{\rho}_{k\mu,l\nu} = i\sum_{i\gamma}[\rho_{k\mu,i\gamma}H_{i\gamma,l\nu} - H_{k\mu,i\gamma}\rho_{i\gamma,l\nu}]. \tag{2.9}$$

The radical pair density matrix element in Eq. (2.9) are formed by the direct product of the free radical elements as follows:

$$\rho_{k\mu,l\nu} = \rho^a_{kl}\times\rho^b_{\mu\nu}. \tag{2.10}$$

In Eqs. (2.8)–(2.10) we have assigned Latin letters (i,j,k,l) to radical a and Greek letters (γ,δ,μ,ν) to radical b.

The core of the problem hinges on the solution of the radical pair density matrix elements $\rho_{k\mu,l\nu}$. Exact solutions of Eq. (2.9) have not to our knowledge been previously reported, perhaps due to the large dimension of these coupled equations (n^4 elements of ρ_e where n is the number of states in the free radical). However, analytic solutions are possible if we simply ignore the nonsecular hyperfine terms in H_e [Eq. (2.6)]. This treatment is valid under the following realistic conditions:

(i) High field limit ($\omega_0 \gg a$): This allows one to consider J interactions of any strength.

(ii) Nonweak exchange ($J \gg a$): This condition does not put any restrictions on the field strength. It also encompasses a range of exchange interactions that are considered weak (i.e., $J \lesssim \omega_0, \tau_e^{-1}$).

Either condition gives the same solution for ρ_e. However, we choose to focus on the high field limit in order to study the exchange interaction over a larger range of values and to benefit from the simple form of the free radical (FR) eigenfunctions. The FR solution in the low field limit requires a transformation to a different basis. However, by this transformation, expressions for the S–T_- mechanism of CIDEP may be uncovered.

To evaluate the Hamiltonian matrix elements in Eqs. (2.8) and (2.9), we begin with the zeroth order free radical basis functions expressed as $|m_S,\Pi_i m_{I,i}\rangle$, where m_S and $m_{I,i}$ are the electron and nuclear spin z-quantum numbers, respectively. The radical pair basis functions are generated by taking all possible products of the free radical basis functions for radicals a and b. The diagonal elements of the H and H_e matrices are trivial to evaluate. Furthermore, since we are working in the high field limit (i.e., $\omega_0 \gg a$), we can ignore the off-diagonal elements of H. What concerns us most here, are the off-diagonal elements of H_e since these are the terms that couple the elements of ρ_e which must be solved. We can express the off-diagonal elements of H_e as

$$\begin{aligned} H_{k\mu,l\nu} &= \langle k\mu|H_e|l\nu\rangle \\ &= \Big\langle m^a_S m^b_S, \prod_i^a m_{I,i}\prod_j^b m_{I,j}|H_e|m^{a'}_S m^{b'}_S, \\ &\quad \times\prod_{i'}^{a'} m_{I,i'}\prod_{j'}^{b'} m_{I,j'}\Big\rangle \\ &= \frac{J}{2}\delta\Big(\prod_i^a m_{I,i},\prod_{i'}^{a'} m_{I,i'}\Big)\delta\Big(\prod_j^b m_{I,j},\prod_{j'}^{b'} m_{I,j'}\Big) \\ &\quad \times\delta(m^a_S,m^{a'}_S \pm 1)\delta(m^b_S,m^{b'}_S \mp 1), \end{aligned} \tag{2.11}$$

where $\delta(x,y) = 1$ for $x = y$ and zero for $x \neq y$.

Encompassed within Eq. (2.11) is the property that a given radical pair state $k\mu$ couples (via J) into no more than one other state. Consequently, the H_e matrix may be transformed so that it block factors into submatrices of dimension no greater than 2×2. It is this feature that enables ρ_e to be solved analytically (cf. the Appendix).

III. EXAMPLES

A. ·RH spin case

We first consider the interaction between identical radicals, each containing a single spin-$\frac{1}{2}$ nucleus. In the high field limit, the basis functions $|m_S,m_I\rangle$ are good eigenfunctions and are chosen in the order $|\alpha,\alpha\rangle$, $|\beta,\alpha\rangle$, $|\alpha,\beta\rangle$, and $|\beta,\beta\rangle$ (i.e., $|1\rangle = |\alpha,\alpha\rangle$, etc.). The ESR spectrum of the ·RH radical has two lines corresponding to transitions between the pairs of states $|1\rangle$, $|2\rangle$ and $|3\rangle$, $|4\rangle$. Since β is the low energy electron spin state, we refer to the transitions as 21 and 43.

The differential equations for the $\rho_{k\mu,l\nu}$ elements of ρ_e follow from Eq. (2.9) and are shown in the Appendix to separate into block factored groups. These groups can be further subfactored so that no more than two differential equations are coupled together. Although this factoring allows solutions to be obtained by standard methods,[27] the algebra is extremely tedious. The approach is outlined in the Appendix for a block factored group. All other groups are solved identically except for changes in indices denoting the different basis functions involved. The appropriate elements $\rho_{k\mu,l\nu}$ are then summed according to Eq. (2.8) and integrated over a distribution of encounter times according to Eq. (2.4). By this (painstaking) procedure, the modified Bloch equations [Eqs. (2.7) and (2.8)] emerge. For ·RH one obtains the following results:

(i) *Longitudinal magnetization*:

$$\dot{M}_{z,kl} = -\frac{1}{T_{1ex}}\left[(M_z - M_z^0)_{kl} - (M_z - M_z^0)_{\mu\nu}\right] + \frac{\omega_1}{\sqrt{2}}(M_+ - M_-)_{kl} - \frac{J}{\tau_f\varphi}\left[\frac{\varphi\tau_e}{1+\varphi^2\tau_e^2}\right]C_{\mu\nu} - \frac{JQ_{\mu\nu}}{\tau_f\varphi^2}\left[\frac{\varphi^2\tau_e^2}{1+\varphi^2\tau_e^2}\right]\left[\frac{\varphi\tau_e}{1+\varphi^2\tau_e^2}\right]D_{\mu\nu}, \tag{3.1}$$

where

$$\frac{1}{T_{1ex}} = \frac{\nu_{ex}}{2} = \frac{J^2}{4\tau_f\varphi^2}\left[\frac{\varphi_2\tau_e^2}{1+\varphi^2\tau_e^2}\right] = \frac{1}{4\tau_f}\left[\frac{J^2\tau^2}{1+\varphi^2\tau^2}\right] \tag{3.2}$$

and

$$C_{\mu\nu} = \mathrm{Im}\,\rho_{kl}\,\rho_{\mu\nu}^* = \mathrm{Im}\,\rho_{kl}\,\rho_{\nu\mu}, \tag{3.3a}$$

$$D_{\mu\nu} = \mathrm{Re}\,\rho_{kl}\,\rho_{\nu\mu}, \tag{3.3b}$$

$$Q_{\mu\nu} = \omega_{kl} - \omega_{\mu\nu} \quad (\pm a \text{ for } \cdot\mathrm{RH} \text{ system}), \tag{3.3c}$$

$$\varphi = \varphi_{\mu\nu} = (J^2 + Q_{\mu\nu}^2)^{1/2}. \tag{3.3d}$$

The reference to $\mu\nu$ denotes transitions other than kl. The designation of $C_{\mu\nu}$, $D_{\mu\nu}$, and $Q_{\mu\nu}$ in terms of $\mu\nu$ reflects the influence of other lines on the behavior of line kl as a result of HSE effects. The exchange frequency ν_{ex} in Eq. (3.2) may be expressed as the product of the exchange probability per encounter P and the encounter frequency τ_f^{-1}.

The Bloch equation for longitudinal magnetization [Eq. (3.1)] accounts for both relaxation (first term) and spin polarization by CIDEP (latter two terms). Spin-exchange relaxation is a cross relaxation process whereby an equal but opposite change occurs in the intensity of the two lines of ·RH (i.e., an exchange of intensity). Consequently, relaxation by spin exchange restores polarized lines not to the Boltzmann level M_z^0, but rather to the average intensity of the two lines. The latter two CIDEP terms in Eq. (3.1) agree with previous theories for high field CIDEP.[13] The significance of these terms and their relation to the rates of relaxation is discussed in paper II.[19]

(ii) *Transverse magnetization*:

$$\dot{M}_{+,kl} = \left[-i(\Delta_{kl} + \delta\nu_{kl}) - \left(\frac{1}{T_{2ex}}\right)_{kl}\right]M_{+,kl} + \frac{\omega_1}{\sqrt{2}}M_{z,kl} + [iI_{\mu\nu} + R_{\mu\nu}]M_{+,\mu\nu}, \tag{3.4}$$

where

$$\delta\nu_{kl} = \frac{1}{2\tau_f}\left\{\frac{\Delta_{kl}\tau_e}{1+\Delta_{kl}^2\tau_e^2} + \left(1+\frac{a}{\varphi}\right)[E_\mu^+\rho_{\mu\mu} + E_\nu^+\rho_{\nu\nu}] + \left(1-\frac{a}{\varphi}\right)[E_\mu^-\rho_{\mu\mu} + E_\nu^-\rho_{\nu\nu}]\right\}, \tag{3.5}$$

$$\frac{1}{T_{2ex}} = \frac{1}{2\tau_f}\left\{\frac{\Delta_{kl}^2\tau_e^2}{1+\Delta_{kl}^2\tau_e^2} + \left(1+\frac{a}{\varphi}\right)[F_\mu^+\rho_{\mu\mu} + F_\nu^+\rho_{\nu\nu}] + \left(1-\frac{a}{\varphi}\right)[F_\mu^-\rho_{\mu\mu} + F_\nu^-\rho_{\nu\nu}]\right\}, \tag{3.6}$$

$$I_{\mu\nu} = \frac{1}{2\tau_f}\frac{J}{\varphi}\{(E_k^- - E_k^+)\rho_{kk} - (E_l^- - E_l^+)\rho_{ll}\}, \tag{3.7}$$

$$R_{\mu\nu} = \frac{1}{2\tau_f}\frac{J}{\varphi}\{(F_k^- - F_k^+)\rho_{kk} - (F_l^- - F_l^+)\rho_{ll}\}, \tag{3.8}$$

and

$$E_\mu^+ = \frac{x_\mu^\pm}{1+(x_\mu^\pm)^2}, \quad F_\mu^\pm = \frac{(x_\mu^\pm)^2}{1+(x_\mu^\pm)^2}, \tag{3.9a}$$

$$x_\mu^\pm = (b_\mu \pm \varphi/2)\tau_e, \quad b_\mu = \begin{cases} b_1 = b_3 = (\Delta_0 + J/2) \\ b_2 = b_4 = (\Delta_0 - J/2) \end{cases}, \tag{3.9b}$$

$$\Delta_{21} = \Delta_0 + \frac{a}{2}, \quad \Delta_{43} = \Delta_0 - \frac{a}{2}. \tag{3.9c}$$

We have defined rotating frame frequencies by $\Delta_{kl} = \omega_{kl} - \omega$ and $\Delta_0 = \omega_0 - \omega$.

The expressions for the HSE induced frequency shift $\delta\nu_{kl}$ and transverse relaxation rate T_{2ex}^{-1} [Eqs. (3.5) and (3.6)] are complicated when generalized for all exchange strengths J. We examine their behavior under limiting conditions shortly. The extent of the coupling of transition $\mu\nu$ to kl is manifested by the terms $I_{\mu\nu}$ and $R_{\mu\nu}$ which contribute, respectively, to the frequency shift and the transverse relaxation rate of transition kl. In Sec. IV B, it is shown that the effective coupling is insignificant under typical ESR conditions since $M_{+,\mu\nu} = 0$ when transition $\mu\nu$ is unexcited. The terms $I_{\mu\nu}$ and $R_{\mu\nu}$, however, become very important for overlapping line conditions resulting, for example, from near degeneracies, field inhomogeneity, or the so-called fast exchange limit ($\nu_{ex} \gtrsim a$) where exchange broadening can cause the coalescence of two (or more) lines (cf. Sec. III A 3).

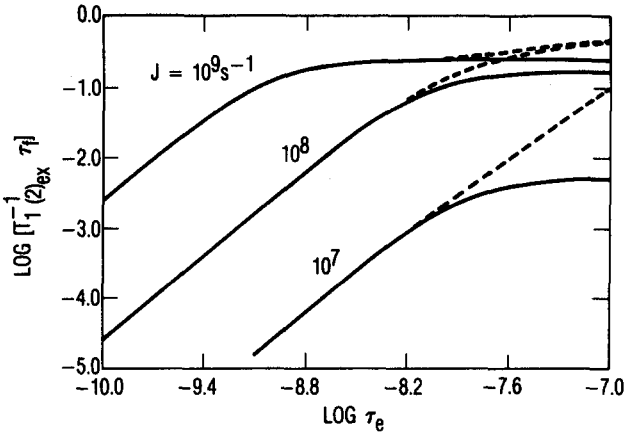

FIG. 1. The rate of longitudinal T_{1ex}^{-1} (—), and transverse T_{2ex}^{-1} (- - -) relaxation as a function of the encounter duration τ_e. The relaxation rates are expressed in terms of a probability per radical pair encounter. Parameters used in calculation: $\Delta_{21}=0$, $\Delta_0=-a/2$, $a=70$ MHz, $\rho_{22}=0.25+\frac{1}{2}\Delta\rho^0$, $\rho_{11}=0.25-\frac{1}{2}\Delta\rho^0$, $\frac{1}{2}\Delta\rho^0=0.0014$. These parameters apply to Figs. 1–4.

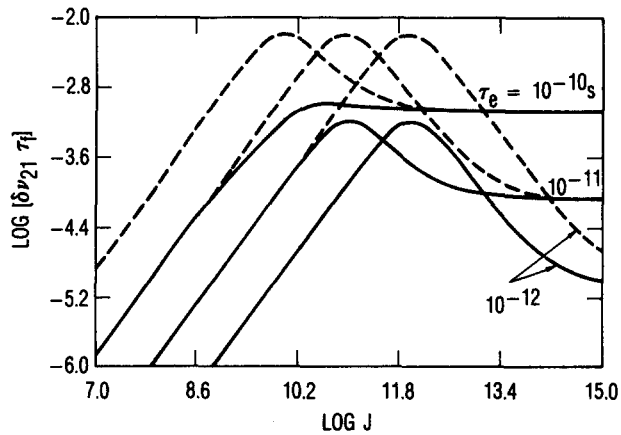

FIG. 2. HSE induced frequency shift $\delta\nu_{21}$ as a function of J for no CIDEP enhancement, $V=0$ (—) and an enhancement of $V=10$ (- - -). The frequency shift in Figs. 2–4 are expressed in terms of a probability per radical pair encounter. See caption to Fig. 1 for parameters used in calculation.

1. Behavior under generalized exchange and viscosity

Equations (3.1)–(3.9) are completely general for all values of J and τ_e (which correlates with viscosity), although at the expense of complexity. The equations reduce considerably in the common limit where $(a/J)^2$, $(\Delta_0\tau_e)^2 \ll 1$ (Sec. III A 2) which holds well in low and medium viscosity solvents. However, before proceeding to a stronger exchange regime, we remark on a few interesting characteristics of Eqs. (3.1)–(3.9). It is instructive to look at two limiting cases of exchange namely $J \ll a$ and $J \gg a$, although all simulations to follow employ the generalized equations. We consider the case for transition $kl=21$ under resonance (i.e., $\Delta_{21}=0$ and $\Delta_0=-a/2$).

(i) *Medium to strong exchange, $J \gg a$:*

$$\delta\nu_{kl}=\frac{1}{2\tau_f}\left\{\frac{J\tau_e}{1+(J\tau_e)^2}(\rho_{\mu\mu}-\rho_{\nu\nu})-\frac{1}{2}\frac{a\tau_e/2}{1+(a\tau_e/2)^2}-\frac{1}{2}\frac{a\tau_e/2}{1+(J\tau_e)^2}\right\}, \tag{3.10}$$

$$\frac{1}{T_{2ex}}=\frac{1}{4\tau_f}\left\{\frac{(J\tau_e)^2}{1+(J\tau_e)^2}+\frac{(a\tau_e)^2/2}{1+(a\tau_e)^2/2}\right\}, \tag{3.11}$$

$$\frac{1}{T_{1ex}}=\frac{1}{4\tau_f}\left\{\frac{(J\tau_e)^2}{1+(J\tau_e)^2}\right\}. \tag{3.12}$$

(ii) *Weak exchange limit, $J \ll a$:*

$$\delta\nu_{kl}=\frac{1}{2\tau_f}\left\{\frac{J\tau_e/2}{1+(J\tau_e)^2/2}(\rho_{\mu\mu}-\rho_{\nu\nu})-\frac{J}{a}\frac{J\tau_e/2}{1+(a\tau_e)^2}\right\}, \tag{3.13}$$

$$\frac{1}{T_{2ex}}=\frac{1}{2\tau_f}\left\{\frac{(J\tau_e)^2/4}{1+(J\tau_e)^2/4}+\frac{(J\tau_e)^2/4}{1+(a\tau_e)^2}\right\}, \tag{3.14}$$

$$\frac{1}{T_{1ex}}=\frac{1}{4\tau_f}\left\{\frac{(J\tau_e)^2}{1+(a\tau_e)^2}\right\}. \tag{3.15}$$

The rates of HSE induced longitudinal and transverse relaxation T_{1ex}^{-1} and T_{2ex}^{-1}, respectively, are essentially equivalent for all values of J under medium to low viscosity conditions which we define as $(a\tau_e)^2 \ll 1$. Under highly viscous conditions (or possibly in biradicals with short chain lengths that restrict separation) T_{2ex}^{-1} becomes greater than T_{1ex}^{-1} as illustrated in Fig. 1. The maximum rate attainable for T_{1ex}^{-1} and T_{2ex}^{-1} is $1/4\tau_f$ and $1/2\tau_f$, respectively, which occurs in the limit where $(a\tau_e)^2$, $(J\tau_e)^2 \gg 1$. These are rather extreme cases and probably not of general significance. In the weak exchange limit, $J \ll a$, T_{2ex}^{-1} is likewise more rapid than T_{1ex}^{-1}. The experimental significance, however, of the weak exchange limit is also probably minor since the small effects that are predicted are bound to be obscured by other relaxation processes not considered here as well as by factors such as slight off-resonance effects (i.e., $\Delta_{kl} \neq 0$) and nonsecular RP hyperfine contributions that are usually taken to be negligible.

In Fig. 2, the frequency shift $\delta\nu_{kl}$ is shown to peak at $J\tau_e$ with a magnitude that depends on the population difference of the transition $\mu\nu$ [cf. Eqs. (3.10) and (3.13)]. We define the observed CIDEP enhancement factor V for an ESR line as $(\Delta\rho-\Delta\rho^0)/\Delta\rho^0$, where $\Delta\rho$ and $\Delta\rho^0$ are the observed and equilibrium (i.e., Boltzmann) population differences, respectively. The frequency shifts are not usually very large,[28] but can become experimentally significant in highly polarized (CIDEP) samples. Also evident in Fig. 2 [and Eq. (3.10)] is a contribution in the $J \gg a$ limit that is a function of $a\tau_e$ and hence may become important in viscous samples. This effect on $\delta\nu_{kl}$ is shown as a function of τ_e in Fig. 3. The hyperfine contribution is clearly a HSE effect since its magnitude is shown to decrease with J (Fig. 3). Finally, we call attention to the region $a \approx J \approx \tau_e^{-1}$ where the frequency shift is predicted to become negative (Fig. 4). This may be viewed as an increase in the *effective* hyperfine splitting. However, the observation would be difficult since the narrow range of conditions is incompatible with the wide distribution of J and τ_e values that typically occur in real systems.

Although unusual effects are predicted at very high vis-

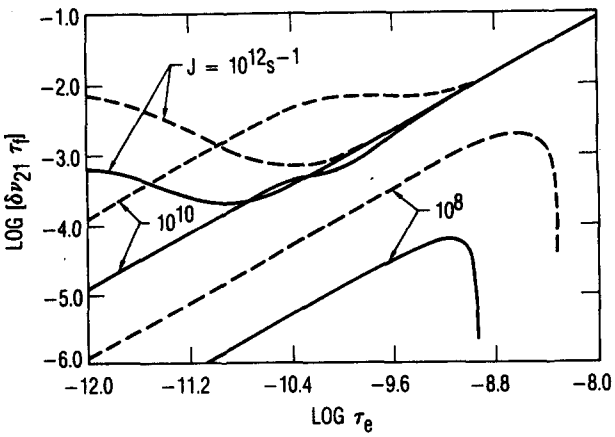

FIG. 3. The frequency shift $\delta\nu_{21}$ as a function of the encounter duration τ_e for $V=0$ (—) and for $V=10$ (- - -).

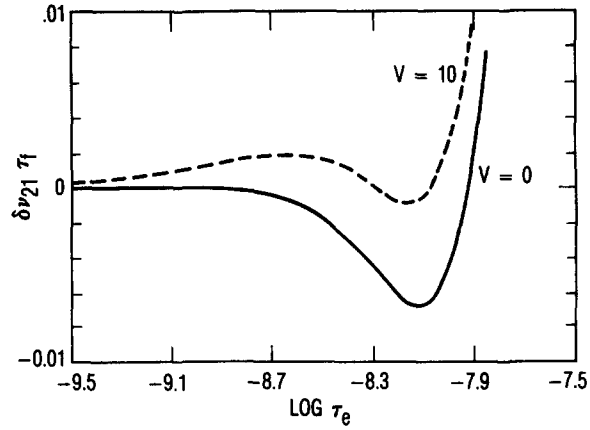

FIG. 4. The frequency shift $\delta\nu_{21}$ as a function of τ_e illustrating the reversal in sign that occurs in the region where $a\approx J\approx\tau_e^{-1}$.

cosity (i.e., $a\tau_e\geqslant 1$) the values of τ_e that have been considered (e.g., $\tau_e\geqslant 10^{-9}\ s^{-1}$) are relatively uncommon in most solution phase studies. Furthermore, if such *long-lived* encounter pairs did exist, then one would have to consider the direct observation of radical pairs, especially if τ_e becomes comparable to the mean time between collisions τ_f. The high viscosity behavior, however, may become important in specific situations such as in soft glasses or in biradicals where the chain lengths can restrict separation and thereby lengthen the encounter times. The effects may also be observed in radicals with unusually large hyperfine splittings (e.g., the H atom[29]) via the $a\tau_e$ term.

2. Intermediate and strong exchange

Most real systems exhibit exchange interactions that are much stronger than those accomodated by Eqs. (3.1)–(3.9). This is a welcomed situation since under the realistic conditions $(J/a)^2$, $(J/\Delta_0)^2\gg 1$, Eqs. (3.1)–(3.9) reduce considerably. If we also assume, quite reasonably for low and medium viscosity solvents that $(a\tau_e)^2\ll 1$, then we obtain the simplified Bloch equations

$$\dot{M}_{+,kl}=-i(\Delta_{kl}+\delta\nu_{kl})M_{+,kl}-\frac{1}{T_{2ex}}M_{+,kl}+\frac{\omega_1}{\sqrt{2}}M_{z,kl}+\left(i\delta\nu_{\mu\nu}+\frac{\nu_{ex}}{2}\right)M_{+,\mu\nu}, \tag{3.16}$$

$$\dot{M}_{z,kl}=-\frac{1}{T_{1ex}}[(M_z-M_z^0)_{kl}-(M_z-M_z^0)_{\mu\nu}]+\frac{\omega_1}{\sqrt{2}}(M_+-M_-)_{kl}-\frac{1}{\tau_f}GC_{\mu\nu}-\frac{2Q_{\mu\nu}}{J}\nu_{ex}GD_{\mu\nu}, \tag{3.17}$$

where

$$\delta\nu_{kl}=\frac{G}{\tau_f}M_{z,\mu\nu}, \tag{3.18}$$

$$\frac{1}{T_{2ex}}=\frac{1}{T_{1ex}}=\frac{\nu_{ex}}{2}, \tag{3.19}$$

and

$$G=\frac{J\tau_e}{1+J^2\tau_e^2}, \tag{3.20}$$

$$\nu_{ex}=\frac{P}{\tau_f}=\frac{1}{2\tau_f}\left[\frac{J^2\tau_e^2}{1+J^2\tau_e^2}\right]. \tag{3.21}$$

The terms ν_{ex} and P represent, respectively, the spin exchange rate and the probability of an exchange per encounter. We note that in the intermediate/strong exchange limit [$(J/a)^2\gg 1$], longitudinal and transverse relaxation become equivalent [Eq. (3.19)].

Equations (3.16)–(3.21) should suffice on a regular basis. The figures presented here (and in paper II[19]) clearly indicate that exchange effects such as relaxation and CIDEP are rather negligible in the limit of weak exchange [i.e., $(J\tau_e)^2\ll 1$]. In fact previous theories routinely consider just strong exchange [i.e., $(J\tau_e)^2\gg 1$], however this condition overlooks the intermediate region $J\tau_e\approx 1$ where CIDEP is most effective. Equations (3.16)–(3.21), on the other hand, extend the range of exchange to the physically interesting region where $J\tau_e\leqslant 1$.

3. Slow vs fast exchange

It has been known for sometime [9–12] that when the exchange frequency ν_{ex} exceeds the frequency difference between lines, that the lines will coalesce and can narrow (motional narrowing) for extremely fast exchange rates. Theories of spin exchange (either nuclear or electron),[8–12,15] therefore, commonly consider two limits referred to as slow and fast exchange. For ·RH, these limits would be marked by the conditions $\nu_{ex}\ll a$ and $\nu_{ex}\gg a$, respectively.

The expressions derived in this paper are fully general and, therefore, valid for a complete range of exchange frequencies. In the above discussion, we implicitly assumed the slow exchange limit, by considering just the *kl* component of the modified Bloch equations. This is legitimate as long as ESR line(s) corresponding to the other component(s) do not overlap with *kl*. This is the case whether the overlap is due to near degeneracy, broadening by fast exchange or any other means. We may, therefore, restate the fast vs slow exchange as the overlapped vs nonoverlapped line condition,

thereby allowing for other factors besides spin exchange. When line kl does not overlap with any other line $\mu\nu$, then the components $M_{+,\mu\nu}$ can be taken to be zero (see Sec. IV B). Consequently, the solution for the transverse magnetization of each line [Eq. (3.4)] becomes decoupled. When overlap occurs (e.g., by fast exchange), then the solution of M_+ for the overlapped lines must be solved as coupled equations.

For systems of reactive radicals, it has not yet been possible to obtain the high radical concentrations required to observe a fast exchange condition. For instance, $a \approx 10^{-3}$ M concentration, which is very high for reactive radicals,[29] would give in the *strong* exchange limit ($J\tau_e \gg 1$) a maximum exchange rate ν_{ex} on the order of $\approx 10^6$ s^{-1}. This is considerably less than typical hyperfine splittings and line separations. Finally, it should be mentioned that at the high concentrations required to observe the limit of fast exchange, intermolecular dipole interactions become important,[30] necessitating a more thorough treatment of relaxation.

B. $\cdot RH_2$ spin case

The treatment of the $\cdot RH_2$ spin case is especially pertinent since it corresponds to a radical system ($\dot{C}H^2CO_2^-$) in which accurate values of spin-exchange frequency[5] and CIDEP enhancement factors[5,24(a),24(c)] were determined. We consider the intermediate to strong exchange case since the weak exchange limit contributes negligibly to relaxation (see Fig. 1) and CIDEP (cf. paper II,[19] Figs. 3–5).

The eight free radical basis functions $|m_S,\Pi_i m_{I,i}\rangle$ for $\cdot RH_2$ are chosen in the order $|\alpha,\alpha\alpha\rangle$, $|\beta,\alpha\alpha\rangle$, $|\alpha,2^{-1/2}(\alpha\beta-\beta\alpha)\rangle$,...$|\beta,\beta\beta\rangle$. Four ESR transitions occur at high field between the pairs of states $|1\rangle,|2\rangle$; $|3\rangle,|4\rangle$; $|5\rangle,|6\rangle$; and $|7\rangle,|8\rangle$ where the two middle transitions are degenerate. The modified Bloch equations for the transitions in $\cdot RH_2$ are given by

$$\dot{M}_{+,kl} = -i(\Delta_{kl}+\delta\nu_{kl})M_{+,kl} - \frac{1}{T_{2ex}}M_{+,kl} + \frac{\omega_1}{\sqrt{2}}M_{z,kl} + \left(i\frac{G}{2\tau_f}M_{z,kl} + \frac{\nu_{ex}}{4}\right)\sum_{\mu\nu\neq kl} M_{+,\mu\nu}, \tag{3.22}$$

$$\dot{M}_{z,kl} = -\frac{1}{T_{1ex}}(M_z - M_z^0)_{kl} + \frac{\nu_{ex}}{4}\sum_{\mu\nu\neq kl}(M_z - M_z^0)_{\mu\nu} + \frac{\omega_1}{\sqrt{2}}(M_+ - M_-)_{kl} + \dot{M}_{z,kl}^{CID}, \tag{3.23}$$

where we now have for the four transition case

$$\delta\nu_{kl} = \frac{G}{2\tau_f}\sum_{\mu\nu\neq kl} M_{z,\mu\nu}, \tag{3.24}$$

$$T_{2ex}^{-1} = T_{1ex}^{-1} = \tfrac{3}{4}\nu_{ex}. \tag{3.25}$$

The CIDEP term, which we have now defined as $\dot{M}_{z,kl}^{CID}$ for shorthand, is given by

$$\dot{M}_{z,kl}^{CID} = -G\sum_{\mu\nu\neq kl}\left\{\frac{1}{\tau_f}C_{\mu\nu} + \frac{2Q_{\mu\nu}}{J}\nu_{ex}D_{\mu\nu}\right\}, \tag{3.26a}$$

$$Q_{\mu\nu} = \omega_{kl} - \omega_{\mu\nu}, \tag{3.26b}$$

$$\Delta_{kl} = \Delta_0 + \sum_i a_i m_{I,i}. \tag{3.26c}$$

The summation over $\mu\nu$ is necessary to account for the additional transitions in $\cdot RH_2$. Otherwise, the CIDEP and other terms, which have been described earlier, are similar to those for $\cdot RH$. We discuss the CIDEP in detail in paper II,[19] but do mention here that the enhancement is a function of $Q_{\mu\nu}$ [Eq. (3.26b)]. Consequently, one finds that the two outer lines of $\cdot RH_2$ (i.e., $kl = 21$ and 87) have opposite polarization since they correspond to the nuclear spin states $\alpha\alpha$ and $\beta\beta$, respectively. For the degenerate transitions ($kl = 43$ and 65), on the other hand, $\dot{M}_{z,kl}^{CID} = 0$ since the summation in Eq. (3.26a) is zero for the nuclear spin states $2^{-1/2}(\alpha\beta-\beta\alpha)$ and $2^{-1/2}(\alpha\beta+\beta\alpha)$ [Eqs. (3.26b) and (3.26c)].

C. General spin case

Finally, we show that modified Bloch equations for HSE may be written to describe radicals with any number of spins. Rather than deal with the individual transitions of the radical, we instead express the equations for each ESR line and incorporate the appropriate degeneracy factors. Furthermore, we make the equations more applicable to time-resolved studies by including phenomenological terms for exchange *independent* relaxation and chemical decay [see Eq. (2.8)]. Here as before, all HSE terms were derived from an exact solution of the RP density matrix and are therefore *not* phenomenological. The set of equations for line λ is given by

$$\dot{M}_{+,\lambda} = -i[\Delta_\lambda + \delta\nu_\lambda(t)]M_{+,\lambda} - \alpha_2(t)M_{+,\lambda} + \frac{\omega_1}{\sqrt{2}}M_{z,\lambda} + \left(i\frac{2w_\lambda G}{\tau_f(t)}M_{z,\lambda} + w_\lambda\nu_{ex}(t)\right)\sum_{\lambda'\neq\lambda} M_{+,\lambda'}, \tag{3.27}$$

$$\dot{M}_{z,\lambda} = -\alpha_1(t)(M_{z,\lambda} - M_{z,\lambda}^0) + w_\lambda\nu_{ex}(t)\sum_{\lambda'\neq\lambda'}(M_{z,\lambda'} - M_{z,\lambda'}^0) + \frac{\omega_1}{\sqrt{2}}(M_+ - M_-)_\lambda + \dot{M}_{z,kl}^{CID}, \tag{3.28}$$

where

$$\delta\nu_\lambda(t) = \frac{2w_\lambda G}{\tau_f(t)}\sum_{\lambda'\neq\lambda} M_{z,\lambda'}, \tag{3.29a}$$

$$\alpha_1(t) = T_{10}^{-1} + T_{1ex}^{-1}(t) + T_R^{-1}(t), \tag{3.29b}$$

$$\alpha_2(t) = T_{20}^{-1} + T_{2ex}^{-1}(t) + T_R^{-1}(t), \tag{3.29c}$$

$$T_{2ex}^{-1}(t) = T_{1ex}^{-1}(t) = (1-w_\lambda)\nu_{ex}(t), \tag{3.29d}$$

$$w_\lambda = \frac{d_\lambda}{\Sigma_\lambda d_\lambda}, \tag{3.29e}$$

and

$$\dot{M}_{z,\lambda}^{CID} = -d_\lambda G\sum_{\lambda'\neq\lambda} d_{\lambda'}\left\{\frac{1}{\tau_f(t)}C_{\lambda'} + \frac{2Q_{\lambda'}}{J}\nu_{ex}(t)D_{\lambda'}\right\}, \tag{3.30a}$$

$$Q_{\lambda'} = \omega_\lambda - \omega_{\lambda'}. \tag{3.30b}$$

We have expressed the degeneracy of line λ (i.e., d_λ) in terms of a relative weight w_λ in Eq. (3.29e). In the case of degenerate lines, the terms C_λ and D_λ must also be summed over the transitions kl and $\nu\mu$ of lines λ and λ' [cf. Eqs. (3.3a) and (3.3b)]. This procedure is illustrated in a detailed discussion of CIDEP in the following paper.[19] The degeneracy effect on relaxation described by Eq. (3.29d) has been known for some time.[12,22] In Sec. IV B, we illustrate a new degeneracy effect that is unique to radicals that exhibit multiplet CIDEP.

IV. APPLICATIONS TO TIME-RESOLVED ESR

A. Implications to reactive radicals

Radicals that exhibit RPM CIDEP are necessarily reactive[13,29] and hence any formulation to describe them should include provisions for chemical decay. We have included a decay term $T_R(t)$ that is generalized for any order reaction, however, we have assumed that reaction (e.g., radical combination) is independent of spin state. For strictly singlet state reactions, the α and β electron spin states are depleted equally and hence the population difference giving rise to the ESR line intensities should presumably remain unchanged. The chemical decay term is then only valid if uncoupled relaxation T_{10}^{-1} is much faster than chemical decay (i.e., $T_{10}^{-1} \gg T_R^{-1}$).[31]

It should be noted that because of chemical decay, other bimolecular processes of the radicals such as the spin-exchange frequency ν_{ex} and polarized magnetization $M_{z,\lambda}^{CID}$ will exhibit time dependence since the encounter frequency τ_f^{-1} decreases with radical concentration $c(t)$. It is convenient then to introduce the relations

$$\nu_e(t) = \tau_f^{-1}(t) = 2k_e c(t), \tag{4.1}$$

$$\nu_{ex}(t) = P\nu_e(t) = 2k_{ex}c(t), \tag{4.2}$$

where k_e and k_{ex} are rate constants for encounter and exchange and the radical concentration $c(t)$ is solved from the general rate expression

$$\dot{c}(t) = T_R^{-1}(t)c(t). \tag{4.3}$$

For second-order chemical decay, one obtains

$$T_R^{-1}(t) = 2k_2 c(t). \tag{4.4}$$

The time dependence of the CIDEP enhancement may likewise be expressed in terms of the radical concentration[5,21,24] by the expression

$$\dot{M}_{z,\lambda}^{CID} = 2E_\lambda M_{z,\lambda}^0 k_2 c(t), \tag{4.5}$$

where E_λ is defined as the intrinsic enhancement factor per reactive RP encounter.[5,19] Rearranging Eqs. (4.5) and (3.30a) and using Eqs. (3.20) and (3.21) and (4.1) and (4.2) gives the important expression

$$E_\lambda(r) = -\frac{k_e G(r)}{k_2 M_z^0} \sum_{\lambda' \neq \lambda} d_{\lambda'}\{C_{\lambda'} + G(r)Q_{\lambda'}\tau_e D_{\lambda'}\}, \tag{4.6}$$

where we have made use of the relation $M_{z,\lambda}^0 = d_\lambda M_z^0$. We note that the expression for $E_\lambda(r)$ in its present form is a function of the RP encounter distance r. The interaction over a distribution of r using an exponential $J(r)$ model will be described in paper II.[19]

B. Solutions of the modified Bloch equations

The coupling of the RP spin states by HSE is manifested by an exchange of ESR line intensities [Eqs. (3.27) and (3.28)]. The system of coupled Bloch equations can be very difficult to solve, especially as the number of ESR lines becomes large. Moreover, the decay of magnetization by relaxation processes including HSE are not in general single exponential. Fortunately, two important conditions allow us to considerably simplify the expressions, and hence the solutions of $M_{+,\lambda}$ and $M_{z,\lambda}$.

(i) In conventional single resonance experiments, only the line of interest λ is excited. The transverse magnetization for all other lines λ' is zero (i.e., $M_{+,\lambda'} = 0$).[32] Hence, the last term in Eq. (3.27) vanishes. The same consideration applies to Eqs. (3.4), (3.16), and (3.22). This treatment assumes that the line that is excited does not overlap with other lines and hence is not applicable to the fast exchange limit (see Sec. III A 3).

(ii) For pure multiplet CIDEP, the *total* magnetization is Boltzmann (i.e., $\Sigma_{\lambda,\lambda'}[M_z - M_z^0] = 0$). In this case, a polarized line will have a non-Boltzmann component that is equal and opposite to that of all other lines combined, i.e.,

$$(M_{z,\lambda} - M_{z,\lambda}^0) = -\sum_{\lambda' \neq \lambda} (M_{z,\lambda'} - M_{z,\lambda'}^0). \tag{4.6a}$$

Substituting Eq. (4.6) into Eq. (3.28) (or into any expression for M_z) simplifies the equations markedly.

The above considerations lead to the following modified Bloch equations:

$$\dot{M}_{+,\lambda} = -i[\Delta_\lambda + \delta\nu_\lambda(t)]M_{+,\lambda} - \alpha_2(t)M_{+,\lambda} + \frac{\omega_1}{\sqrt{2}} M_{z,\lambda}, \tag{4.7}$$

$$\dot{M}_{z,\lambda} = -\alpha_1^{eff}(t)[M_{z,\lambda} - M_{z,\lambda}^0] + \dot{M}_{z,kl}^{CID} + \frac{\omega_1}{\sqrt{2}}(M_+ - M_-)_\lambda, \tag{4.8}$$

where $\delta\nu_\lambda(t)$ and $\alpha_2(t)$ are given in Eqs. (3.29) and where we have defined an effective decay function as

$$\alpha_1^{eff}(t) = \alpha_1(t) + w_\lambda \nu_{ex}(t). \tag{4.9}$$

Conditions (i) and (ii) above are by no means restrictive. Pure multiplet CIDEP is observed in high fields when a single radical species dominates, which is a common situation. Likewise, condition (i) holds whenever the observed line does not overlap with any other lines.

The decay terms $\alpha_1^{eff}(t)$ and $\alpha_2(t)$ consist of the processes of exchange independent relaxation, HSE induced relaxation, and chemical decay. It is interesting to note, however, that the effective decay function α_1^{eff} in Eq. (4.9) differs from α_1 in Eq. (3.29b) by an additional spin-exchange term. The effective HSE longitudinal relaxation rate is therefore given by $(T_{1ex}^{-1})_{eff} = T_{1ex}^{-1} + w_\lambda \nu_{ex}$, whereas for transverse relaxation, $(T_{2ex}^{-1})_{eff} = T_{2ex}^{-1}$. Using Eqs. (3.29), we obtain the relation

$$\left(\frac{T_{1ex}}{T_{2ex}}\right)_{eff} = 1 - w_\lambda, \tag{4.10}$$

which predicts that longitudinal relaxation is faster than transverse relaxation. This unusual behavior, however, is a special case attributable to multiplet polarization. As mentioned earlier, a manifestation of HSE is an exchange of intensity between dif-

ferent lines. Hence, if two exchanging lines are oppositely polarized, then a given line λ will not only lose one unit of intensity by HSE, but will also acquire a unit of opposite intensity from another line λ' thus contributing further to the loss of intensity in line λ.

An analytic solution of the Bloch equations in Eqs. (4.7) and (4.8) is possible in the limit where $\alpha_1, \alpha_2 \gg \omega_1$. This condition is rigorously valid for pulsed ESR where the excitation field is off during the time evolution of the radical magnetization and valid for cw experiments for low power excitation fields. Using standard methods[27] one obtains

$$M_{+,\lambda}(t) = k(t,0) r_2(t,0)\, M_{+,\lambda}(0) \times \exp\{-i[\Delta_\lambda + \delta\nu_\lambda(t)]\}, \tag{4.11}$$

$$M_{z,\lambda}(t) = k(t,0)\{r_1(t,0)[M_{z,\lambda}(0) - M^0_{z,\lambda}(0)] + [1 + \Lambda_\lambda(t,0)] M^0_{z,\lambda}(0)\}, \tag{4.12}$$

where

$$r_{1(2)}(t,0) = \exp\left[-\int_0^t T^{\text{eff}}_{1(2)}(t')^{-1}\, dt'\right], \tag{4.13a}$$

$$T_1^{\text{eff}}(t)^{-1} = T_{10}^{-1} + \nu_{\text{ex}}(t), \tag{4.13b}$$

$$T_2^{\text{eff}}(t)^{-1} = T_2(t)^{-1} = T_{20}^{-1} + (1 - w_\lambda)\nu_{\text{ex}}(t), \tag{4.13c}$$

$$\Lambda_\lambda(t,0) = 2E_\lambda k_2 c(0) \int_0^t k(t',0) r_1(t,t')\, dt', \tag{4.13d}$$

$$k(t,0) = \exp\left[\int_0^t T_R(t')^{-1}\, dt'\right] = \frac{c(t)}{c(0)}. \tag{4.13e}$$

If the initial longitudinal magnetization is at equilibrium, then the term $[M_{z,\lambda}(0) - M^0_{z,\lambda}(0)]$ in Eq. (4.12) disappears. This term, therefore, accounts for polarization that might occur by mechanisms other than RP CIDEP (e.g., the triplet mechanism[22]). The above equations do not include ω_1 since we assumed the low power limit.

The expressions for the time-dependent magnetization of transient radicals given here are more general than previous approaches[5,22–24] in the sense that they consider relaxation processes that (i) are bimolecular and therefore concentration and time dependent, (ii) couple different lines in an ESR spectrum, and (iii) have unequal rates of longitudinal and transverse relaxation. The equations also treat RPM CIDEP and chemical decay in a realistic way.

V. SUMMARY AND CONCLUSION

A formalism for Heisenberg spin exchange (HSE) has been developed which relates the process of RPM CIDEP and relaxation. An exact solution of the radical pair density matrix, incorporating all spin states of a generalized spin system, was obtained by invoking realistic conditions. The results have been formulated in terms of modified Bloch equations and have been worked out for the ·RH, ·RH_2, and general n-line spin case. Expressions which are continuous from the weak ($J \ll a$) to the strong ($J \gg a$) exchange limit are given for the relaxation rates $T_{1\text{ex}}^{-1}$, $T_{2\text{ex}}^{-2}$ and the frequency shift $\delta\nu_{kl}$. The theory is also completely general for all viscosities, although limiting cases are explored.

It is shown that the normally very weak frequency shifts are strongly enhanced by CIDEP, although their magnitudes may still be difficult to observe. The theory also predicts a rather interesting HSE relaxation effect in radical systems that exhibit multiplet type CIDEP. Time-resolved ESR studies should show an observed longitudinal relaxation rate that is faster than the transverse rate by an amount that depends on the degeneracy of the observed line vs the total number of transitions of the radical.

The framework for HSE presented in this paper has been adapted to describe time-resolved ESR experiments of reactive radicals. In this regard, the solutions of the modified Bloch equations are capable of treating (1) instantaneous and RPM CIDEP, (2) coupled and time dependent relaxation by HSE, and (3) second-order chemical decay.

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APPENDIX: SOLUTIONS OF THE RADICAL PAIR DENSITY MATRIX ELEMENTS

We present the details of the solution $\rho_{k\mu,l\nu}$ [Eq. (2.9)] for the ·RH radical with transitions $kl = 21$ and 43 (Sec. III A). Extensions to larger spin systems involve identical methods of solution, but require more elements to account for the greater number of transitions. The solution of the RP density matrix elements $\rho_{k\mu,l\nu}$ according to Eq. (2.9) may be divided into two groups corresponding to elements required for describing (1) longitudinal relaxation and CIDEP and (2) transverse relaxation.

1. Longitudinal terms, $\rho_{k\mu,k\mu}$, $k = 1$ to 4

The elements required for the description of $\dot{M}_{z,kl}$ encompassing longitudinal relaxation and polarization by CIDEP are of the form $\rho_{k\mu,k\mu}$ [Eqs. (2.7c) and (2.8)]. By operating on the basis set for ·RH (Sec. III A) and using Eqs. (2.5) and (2.6) and (2.11) one obtains for these and their coupled elements by Eq. (2.9) the following equations:

$$\dot{\rho}_{11,11} = \dot{\rho}_{13,13} = \dot{\rho}_{22,22} = \dot{\rho}_{24,24} = 0, \tag{A1}$$

$$\dot{\rho}_{12,12} = \frac{iJ}{2}(\rho_{12,21} - \rho_{21,12}), \tag{A2a}$$

$$\dot{\rho}_{12,21} = \frac{iJ}{2}(\rho_{12,12} - \rho_{21,21}), \tag{A2b}$$

$$\dot{\rho}_{21,12} = \frac{iJ}{2}(\rho_{21,21} - \rho_{12,12}), \tag{A2c}$$

$$\dot{\rho}_{21,21} = \frac{iJ}{2}(\rho_{21,12} - \rho_{12,21}), \tag{A2d}$$

$$\dot{\rho}_{14,14} = \frac{iJ}{2}(\rho_{14,23} - \rho_{23,14}), \tag{A3a}$$

$$\dot{\rho}_{14,23} = \frac{iJ}{2}(\rho_{14,14} - \rho_{23,23}) - ia\rho_{14,23}, \tag{A3b}$$

$$\dot{\rho}_{23,14} = \frac{iJ}{2}(\rho_{23,23} - \rho_{14,14}) + ia\rho_{23,14}, \tag{A3c}$$

$$\dot{\rho}_{23,23} = \frac{iJ}{2}(\rho_{23,14} - \rho_{14,23}). \tag{A3d}$$

The solution of Eq. (A1) is trivial, simply being

$$\rho_{\kappa\mu,\kappa\mu}(t) = \rho_{k\mu,k\mu}(0), \quad \kappa\mu = 11,13,22,24. \tag{A4}$$

The differential equations in Eqs. (A2) and (A3) have been factored into two fourth rank equations. These equations, however, have a common form which may be factored further.[8(b),17] The solutions may then be expressed in matrix form[27] as

$$\sigma(t) = U(t,0)\sigma(0), \tag{A5a}$$

$$U(t,0) = 1 - \frac{\sin\phi t}{\phi} M + \frac{\sin^2 \phi t/2}{\phi^2/2} M^2, \tag{A5b}$$

where t is the duration of an encounter and where the following sets of terms are to be inserted:

$$\sigma = \begin{pmatrix} \rho_{12,12} \\ \rho_{12,21} \\ \rho_{21,12} \\ \rho_{21,21} \end{pmatrix},$$

$$M = \begin{pmatrix} 0 & \frac{J}{2} & -\frac{J}{2} & 0 \\ \frac{J}{2} & 0 & 0 & -\frac{J}{2} \\ -\frac{J}{2} & 0 & 0 & \frac{J}{2} \\ 0 & -\frac{J}{2} & \frac{J}{2} & 0 \end{pmatrix}, \quad \phi = J, \tag{A6a}$$

$$\sigma = \begin{pmatrix} \rho_{14,14} \\ \rho_{14,23} \\ \rho_{23,14} \\ \rho_{23,23} \end{pmatrix},$$

$$M = \begin{pmatrix} 0 & \frac{J}{2} & -\frac{J}{2} & 0 \\ \frac{J}{2} & -a & 0 & -\frac{J}{2} \\ -\frac{J}{2} & 0 & a & \frac{J}{2} \\ 0 & -\frac{J}{2} & \frac{J}{2} & 0 \end{pmatrix},$$

$$\phi = (J^2 + a^2)^{1/2}. \tag{A6b}$$

In the strong exchange limit ($J \gg a$) the forms of M and ϕ in Eqs. (A6a) and (A6b) become equivalent. The solution for $kl = 43$ is obtained by replacing 21 with 43 and $-a$ with a.

2. Transverse terms, $\rho_{k\mu,k\mu}$, $kl = 21, 43$

The RP density matrix elements required to solve for transverse magnetization $M_{+,kl}$ are of the form $\rho_{l\mu,k\mu}$ [Eqs. (2.7a) and (2.8)]. We express these and their coupled elements for transition $kl = 21$ in a notation similar to that used by Johnson[11]:

$$a_{12}^{+} = \rho_{11,21}, \quad b_{12}^{+} = \rho_{11,12}, \quad c_{12}^{+} = \rho_{13,23}, \quad d_{12}^{+} = \rho_{13,14},$$
$$a_{12}^{-} = \rho_{12,22}, \quad b_{12}^{-} = \rho_{21,22}, \quad c_{12}^{-} = \rho_{14,24}, \quad d_{12}^{-} = \rho_{23,24}. \tag{A7}$$

The matrix elements above have been factored to give doubly coupled sets of differential equations which follow from Eqs. (2.5) and (2.6) and (2.9)–(2.11) giving

$$\dot{a}_{12}^{\pm} = -i\left[\omega_0 \pm \frac{J}{2} + \frac{a}{2}\right] a_{12}^{\pm} \pm \frac{iJ}{2} b_{12}^{\pm}, \tag{A8a}$$

$$\dot{b}_{12}^{\pm} = -i\left[\omega_0 \pm \frac{J}{2} + \frac{a}{2}\right] b_{12}^{\pm} \pm \frac{iJ}{2} a_{12}^{\pm}, \tag{A8b}$$

$$\dot{c}_{12}^{\pm} = -i\left[\omega_0 \pm \frac{J}{2} + \frac{a}{2}\right] c_{12}^{\pm} \pm \frac{iJ}{2} d_{12}^{\pm}, \tag{A9a}$$

$$\dot{d}_{12}^{\pm} = -i\left[\omega_0 \pm \frac{J}{2} - \frac{a}{2}\right] d_{12}^{\pm} \pm \frac{iJ}{2} c_{12}^{\pm}. \tag{A9b}$$

The solutions of the doubly coupled equations in Eqs. (A8) and (A9) may likewise be expressed in compact matrix form[27] as

$$\sigma^{\pm}(t) = U^{\pm}(t,0)\,\sigma^{\pm}(0), \tag{A10}$$

where we have

$$U^{\pm}(t,0) = e^{-\Phi^{\pm} t}\left[\left(\cos\frac{\phi t}{2} - i\frac{a}{\phi}\sin\frac{\phi t}{2}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \pm \left(\frac{iJ}{\phi}\sin\frac{\phi t}{2}\right)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right], \tag{A11}$$

where

$$\Phi^{\pm} = \omega_0 \pm \frac{J}{2}, \tag{A12}$$

and where the following sets of terms apply:

$$\sigma^{\pm} = \begin{pmatrix} a_{12}^{\pm} \\ b_{12}^{\pm} \end{pmatrix}, \quad \phi = J, \tag{A13a}$$

$$\sigma^{\pm} = \begin{pmatrix} c_{12}^{\pm} \\ d_{12}^{\pm} \end{pmatrix}, \quad \phi = (J^2 + a^2)^{1/2}. \tag{A13b}$$

As was true for the longitudinal elements, one has $\phi = J$ in the strong exchange limit ($J \gg a$). Likewise, the solution for the $kl = 43$ transition is obtained by replacing 21 with 43 and $-a$ with a.

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[31]I thank R. G. Lawler and A. D. Trifunac for discussing their work regarding this effect.
[32]It would appear at first that coherence from line λ can be imparted to line λ' by the exchange of spins, thus making $M_{+,\lambda\cdot}$ nonzero. However, since the magnetization for lines λ and λ' precess about the applied field at different frequencies ($\Delta_\lambda - \Delta_{\lambda'}$), a phase coherence for one line would appear random in the rotating frame of the other line.