TRANSIENT SOLUTION OF A SPIN EXCHANGE MODEL: CORRESPONDENCE BETWEEN CIDEP AND RELAXATION

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A procedure for relating CIDEP and relaxation in a Heisenberg spin exchange (HSE) model is presented which considers all the spin states of a radical pair. The method relies on an exact (transient) solution of the radical pair density matrix under realistic assumptions and is illustrated for the simple ·RH spin case. The results are cast in the form of Bloch-type equations and are suitable for describing time-resolved ESR experiments.

1. Introduction

The exchange interaction between the electron spins of free radicals can give rise to the processes of relaxation and polarization (CIDEP). The disparate nature of these effects arises since they operate over very different distributions of the exchange strength, J. Relaxation is dominant for strong interactions ($J\tau_e \gg 1$, where τ_e is an effective encounter duration) whereas CIDEP is most efficient for weak to intermediate exchange ($J\tau_e \leqslant 1$) [1]. Since CIDEP and relaxation by spin exchange are also best formulated in a different electron spin basis set, the two processes have always been treated separately.

The first theories of Heisenberg spin exchange (HSE) were concerned with T_2 measurements from cw ESR experiments [2] and hence were derived in terms of lineshape functions using steady state solutions [2–4]. Adaptations to saturation recovery and ELDOR experiments to describe T_1 measurements soon followed these initial developments [5]. In all cases, the theories applied to unreactive radicals and hence resembled approaches taken to describe chemical exchange effects in NMR [6].

Theories of radical pair CIDEP exist at many levels of rigor [7–11]. However, in virtually all instances, the high-field limit is employed so as to reduce the problem to just two radical pair electron spin states (i.e. S and T_0). Relaxation effects have been treated within this basis and are referred to as polarization quenching [10]. However, the S, T_0 basis ignores the $\alpha\alpha$ and $\beta\beta$ electron spin states which are critical to a complete description of relaxation by HSE.

The intent of this paper is to outline a unified approach to relaxation and CIDEP that considers all the spin states of a pair of radicals. The procedure begins with a conventional method for modelling exchange-type processes, but instead relies on an exact (transient) solution of the encounter pair density matrix which is made possible by invoking realistic assumptions. The present treatment applies to reactive radicals and is cast in terms of Bloch-type equations suitable for time-resolved studies using pulsed ESR.

2. General equations

A general method for representing the density matrix equations of motion for two spin systems that undergo exchange-type processes [12] is given by

$$\dot{\rho} = \dot{\rho}_{\text{exch}} + \mathrm{i}[\rho, H] + R\rho, \tag{1}$$

$$\dot{\rho}_{\text{exch}} = \tau_f^{-1}(\tfrac{1}{2}\langle \mathrm{Tr}^b\rho_e + \mathrm{Tr}^a\rho_e\rangle - \rho), \tag{2}$$

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$$\dot{\rho}_e = i[\rho_e, H_e], \tag{3}$$

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. The brackets $\langle\ \rangle$ designate an average over some distribution of encounter times. We assume that $\tau_f \gg \tau_e$ to indicate that the free radicals and not the radical pairs are the observed species.

The free radical and radical pair spin Hamiltonians (in Hz) in a magnetic field are given, respectively, by

$$H^a = \nu_0 S_z^a - \nu_n \sum_{i=0}^{a} I_{zi} + \sum_{i=0}^{a} a_i \boldsymbol{I}_i \cdot \boldsymbol{S}^a, \tag{4}$$

$$H_e = H^a + H^b + J\boldsymbol{S}^a \cdot \boldsymbol{S}^b, \tag{5}$$

where $J/2$ is the negative of the exchange integral, ν_0 is the Larmor frequency of the electron spins and a_i are the hyperfine splittings. We express the nuclear spin frequency by a single term ν_n 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, ν_0, J).

In the present treatment we consider equivalent radicals and have therefore symmetrized the trace operation in eq. (2). Alternatively, we may focus on a single free radical (i.e. a) of the radical pair and sum over the states of the partner radical (i.e. b). Identical results have been obtained by these two approaches, however, we find it easier to express the equations in the latter form. The elements of ρ for the free radical may then be described by

$$\dot{\rho}^a_{kl} = \tau_f^{-1}\left(\left\langle \sum_\mu \rho_{k\mu,l\mu} \right\rangle - \rho_{kl}\right) + i \sum_m (\rho_{km} H_{ml} - H_{km}\rho_{ml}) - [(\rho_{kl} - \rho^0_{kl})/T_{1_0}]_{k=l} - (\rho_{kl}/T_{2_0})_{k\neq l} - \rho_{kl}/T_{R,kl}(t), \tag{6}$$

where ρ_{kl} on the rhs refers to radical a. Phenomenological terms have also been included for exchange-independent relaxation, $T_{1_0}^{-1}$ and $T_{2_0}^{-1}$, and spin-dependent reaction probabilities, $T_{R,kl}^{-1}(t)$. In subsequent expressions we will exclude the phenomenological terms since they are not directly involved in the solution or behavior of exchange effects. The corresponding set of equations for the encounter radical pair are given by

$$\dot{\rho}_{k\mu,l\nu} = i \sum_{i\gamma} (\rho_{k\mu,i\gamma} H_{i\gamma,l\nu} - H_{k\mu,i\gamma}\rho_{i\gamma,l\nu}). \tag{7}$$

The radical pair density matrix elements in eq. (7) are formed by the direct product of the free radical elements as follows

$$\rho_{k\mu,l\nu} = \rho^a_{kl} \times \rho^b_{\mu\nu}. \tag{8}$$

In eqs. (6)–(8) we have assigned italic letters (i, j, k, l) to radical a and Greek letters (γ, δ, μ, ν) to radical b.

We are not aware of any exact solutions of eq. (7) for realistic size spin systems either for want of need or presumably due to the large dimension of these coupled equations (n^4 elements of ρ_e, where n is the number of spin states in the free radical). However, analytic solutions are possible if we simply ignore the non-secular hyperfine terms in H_e (eq. (5)). This treatment becomes valid by invoking one of the following realistic conditions: (1) high-field limit ($\nu_0 \gg a$) which allows one to consider any value for the exchange strength, J or (2) non-weak exchange ($J \gg a$) which allows for low-field cases. Both conditions give the same solution for ρ_e. However, we choose to focus on the high-field limit since it is valid over a larger range of exchange interactions and leads to a diagonal Hamiltonian matrix for the free radical in eq. (6).

The Hamiltonian matrix elements in eqs. (6) and (7) are evaluated using 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. Under the conditions described above, the radical pair density matrix may be block factored enabling analytic (though tedious) solutions [13,14]. The initial condition $\rho_{k\mu,l\nu}(0)$ that emerges from the solution is given by the direct product of the free radical density matrix elements according to eq. (8). The solution of ρ_e is then summed over the states of radical b (eq. (6)) and averaged over the distribution of encounter times. We use an exponential translational correlation function for radical pair separation and hence average

$$D_{\mu\nu} = (\rho_{SS,\chi I} - \rho_{T_0T_0,\chi I}), \tag{14b}$$

where χ_I denotes the radical pair nuclear spin state. The terms in eqs. (14) have been related to radical pair diffusion models in earlier theories of CIDEP [7] and will be elaborated upon in the context of this theory in another paper [13]. We do mention that the first CIDEP term in eq. (11) is most responsible for radical pair CIDEP; the second term contributes a negligible effect [7].

3.2. Intermediate and strong exchange interactions

Most real systems exhibit exchange interactions that satisfy the realistic conditions $(J/a)^2, (J/\nu_0)^2 \gg 1$. If we also assume, quite reasonably for non-viscous solutions, that $(\nu_0\tau_e)^2 \ll 1$, then the Bloch equations reduce considerably to

$$\dot{M}_{+,kl} = -i(\nu_{kl} + \delta\nu_{kl})M_{+,kl} - T_{2ex}^{-1} M_{+,kl} + (i\tau_f^{-1} G M_{z,kl} + \tfrac{1}{2}\nu_{ex})M_{+,\mu\nu}\ , \tag{15}$$

$$\dot{M}_{z,kl} = -T_{1ex}^{-1}[(M_z - M_z^0)_{kl} - (M_z - M_z^0)_{\mu\nu}] - \tau_f^{-1} G C_{\mu\nu} - (2\Omega_{\mu\nu}/J)\nu_{ex} G D_{\mu\nu}, \tag{16}$$

where

$$\delta\nu_{kl} = \tau_f^{-1} G M_{z,\mu\nu}, \tag{17a}$$

$$T_{2ex}^{-1} = T_{1ex}^{-1} = \tfrac{1}{2}\nu_{ex} \tag{17b}$$

and

$$G = J\tau_e/(1 + J^2\tau_e^2), \tag{18a}$$

$$\nu_{ex} = \tau_f^{-1} P = \tfrac{1}{2}\tau_f^{-1}[J^2\tau_e^2/(1 + J^2\tau_e^2)]. \tag{18b}$$

We note that in the intermediate/strong exchange limit ($(J/a)^2 \gg 1$), longitudinal and transverse relaxation by HSE become equivalent (eq. (17b)), unlike in the very weak exchange regime [13].

The use of eqs. (15)–(18) on a general basis is quite justified since exchange effects such as relaxation and CIDEP are rather negligible in the limit of very weak exchange (i.e. $(J\tau_e)^2 \ll 1$). In fact previous theories routinely considered just strong exchange under the condition $(J\tau_e)^2 \gg 1$, however this treatment overlooks the intermediate region $J\tau_e \approx 1$ where CIDEP is most effective. Eqs. (15)–(18), on the other hand, extend the range of exchange to the physically interesting region, $J\tau_e \leqslant 1$.

4. Conclusion

A framework for relating CIDEP and relaxation by the exchange interaction that considers all the spin states of a radical pair has been outlined. The radical pair density matrix for a Heisenberg spin exchange (HSE) model has been solved exactly in the high field limit for the ·RH spin case. Extensions to larger systems are possible [13,14]. The equations have been formulated in terms of Bloch-type equations making them suitable for time-resolved ESR studies of reactive radicals [15–17]. Recent techniques [16], which now enable one to concurrently measure both CIDEP enhancements and relaxation rates by HSE [14,17], attest to the need to unify our understanding of these two processes.

In a subsequent publication [13] the Bloch-type equations will be generalized for n-spin (or n-ESR line) systems and incorporate phenomenological terms for HSE independent relaxation and chemical decay. It will also be shown how the spin exchange frequency and the CIDEP enhancement factor can be averaged over a distance dependent exchange interaction (i.e. $J(r)$) to give more realistic yet analytic expressions.

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