A VECTOR MODEL FOR CIDEP: THE ROLE OF THE EXCHANGE INTERACTION

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Received 22 June 1982

A vector model is presented which illustrates the role of the exchange interaction in CIDEP and relaxation. The vector representations of the S and T_0 radical pair states are constructed to have the same properties of angular momentum and symmetry as the corresponding wavefunctions. Applications of the vector model to net and multiplet CIDEP and to polarization quenching are discussed.

1. Introduction

Throughout science one frequently encounters situations where a theoretically well understood subject conveys little or no physical intuition. This problem certainly holds true for chemically induced magnetic polarization. Although convenient vector models are available to explain chemically induced dynamic nuclear polarization (CIDNP) [1], far less success has been achieved in developing a physical picture for the more complicated, but related phenomenon of electron spin polarization (CIDEP) [1,2]. In this paper we present a vector model that predicts all the qualitative features of high-field radical pair CIDEP [1,2]. The present model starts out similarly to that of Atkins [3], however, we correct his vector representation of the singlet state and adopt an entirely different approach to explain the role of the exchange interaction in CIDEP. Another recent vector model for CIDEP by Adrian and Monchick [4] employs a semiquantitative approach and hence is notably more difficult to visualize than the present model.

2. S and T_0 state vector representations

Atkins [3] has pointed out that the conventional vector representations of the singlet (S) and triplet (T_0) states used for describing CIDNP [1] are deficient and inadequate for explaining CIDEP. The complete vector representations must have the same properties as the S and T_0 state wavefunctions in regard to angular momentum,

$$\mathbf{S}^2|\psi\rangle = s(s+1)\hbar^2|\psi\rangle, \tag{1}$$

$$\mathbf{S}_z|\psi\rangle = m_s\hbar|\psi\rangle, \tag{2}$$

and symmetry,

$$\mathbf{P}|\psi\rangle = p|\psi\rangle, \quad p = +1, \text{ symmetric state}, \quad = -1, \text{ antisymmetric state}. \tag{3}$$

In eqs. (1)–(3), $\mathbf{S}$ and $\mathbf{S}_z$ are the total and z component operators of angular momentum, respectively, and $\mathbf{P}$ is the permutation operator for the radical pair electron spins. The properties of the S and T_0 wavefunctions according to the above equations are summarized in table 1 and the correct vector representations are illustrated in fig. 1.

There are actually two S state vector designations which satisfy the angular momentum and permutation

Table 1
Properties of angular momentum and symmetry

State	Wavefunction	s	m_s	p
S	$2^{-1/2}(\alpha_a\beta_b - \beta_a\alpha_b)$	0	0	−1
T_0	$2^{-1/2}(\alpha_a\beta_b + \beta_a\alpha_b)$	1	0	1

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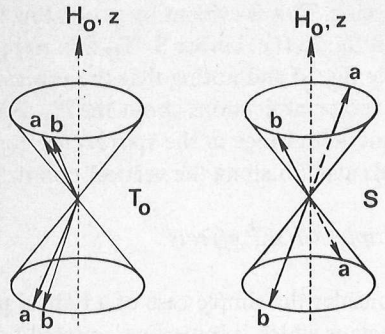

Fig. 1. Vector representations of the T_0 and S states for radicals a and b of a radical pair. The higher energy electron spin state α is defined along the positive z axis where H_0 denotes the applied magnetic field.

properties in table 1; that given in fig. 1 and a corresponding one [3] in which the labels a and b along one of the cones are reversed. Only the former designation, however, obeys the properties of transverse momentum for a single electron spin

$$\mathbf{S}_{x,a}|S\rangle = 2^{-3/2}\hbar(|\beta_a\beta_b\rangle - |\alpha_a\alpha_b\rangle) = -\mathbf{S}_{x,b}|S\rangle, \quad (4)$$

$$\mathbf{S}_{y,a}|S\rangle = i2^{-3/2}\hbar(|\beta_a\beta_b\rangle + |\alpha_a\alpha_b\rangle) = -\mathbf{S}_{y,b}|S\rangle, \quad (5)$$

where $\mathbf{S}_{x,i}$ and $\mathbf{S}_{y,i}$ are the x and y component operators of angular momentum, respectively, for the unpaired electron spin on radical i = a or b of the radical pair [‡]. Naturally, the *total* angular momentum of a singlet state radical pair is zero.

3. Applications of the vector model

The simplest diffusive scheme for explaining radical pair CIDEP is given by a separation of the initially formed radical pair followed by a re-encounter of the *same* pair. We assume that these two intervals are marked, respectively, by the conditions $|J| \ll |\delta_n|$ and $|J| \gg |\delta_n|$, where J is the short-range exchange interaction and δ_n is the S–T_0 mixing coefficient given by the difference in the precession frequencies, ν_i, of the electron spin vectors of radicals a and b,

$$\delta_n\,(\mathrm{Hz}) = \nu_a - \nu_b = \frac{1}{2}\Big[(1/2\pi)(g_a - g_b)\,\gamma_e H_0 + \sum_j^a A_j m_{I,j} + \sum_k^b A_k m_{I,k}\Big]. \quad (6)$$

The terms g_i, γ_e and H_0 denote the g factor, magnetogyric ratio and the applied magnetic field. A and m_I represent hyperfine splittings and nuclear spin z-quantum numbers, respectively. We note that the exchange hamiltonian given by $J\mathbf{S}_1\cdot\mathbf{S}_2$ is analogous in form to that of the hyperfine interaction, $A\,\mathbf{I}\cdot\mathbf{S}$. Since the latter effect represents the interaction of the magnetic fields of a nuclear and electron spin with each other, we may regard the corresponding exchange interaction as the mutual influence of the magnetic fields of the radical pair electron spins. This may be viewed as a precession of the electron spin vectors about each other, which is effectively the same as a rotation about their resultant axis. We define this resultant axis as the exchange field axis, H_e.

To predict the qualitative features of CIDEP, one simply follows the precession of the spin vectors in fig. 1 about the applied field H_0 axis at frequency δ_n during the diffusive separation and about the spin vector resultant axis H_e at frequency J during the re-encounter period. We illustrate this procedure for various cases below. In so doing, we define the higher energy electron spin state α along the positive H_0 axis. We also assume that the exchange interaction is inherently negative (i.e. $J = -|J|$) as is true for the electron spin magnetogyric ratio, γ_e. Consequently, the spin vectors precess about the H_0 and H_e axes in the same sense; we choose counterclockwise. If J is positive, however, the direction of precession about the two axes will be counter to each other, thus predicting opposite polarization (see later), in agreement with theory [2].

3.1. Net CIDEP effects

We illustrate the use of the model to visualize the development of net polarization by considering a radical pair that is initially in the T_0 state and which has no hyperfine interactions. During the diffusive separation period, under the condition $|\delta_n| \gg |J|$, the precession of the spin vectors occurs about the applied field H_0 axis. For $g_a > g_b$ it is clear that the spin vector for radical a precesses faster than that for radical b (δ_n

[‡] Eqs. (4) and (5) demonstrate that each electron spin of an S state radical pair has transverse angular momentum that is opposite to each other, a property not exhibited by Atkins' [3] S state vector designation.

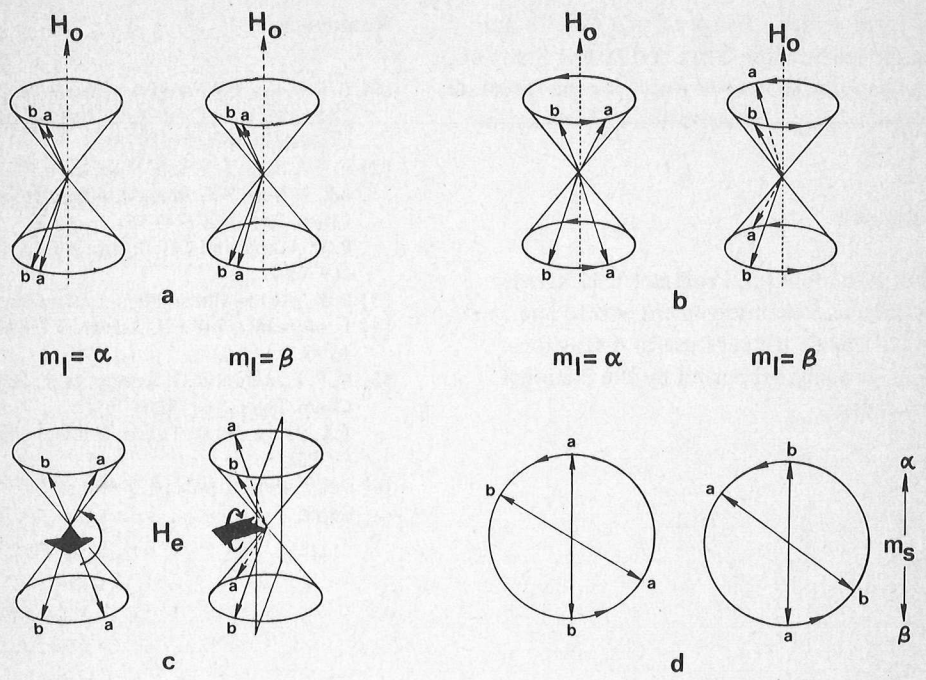

Fig. 3. Vector model for CIDEP multiplet effects. Initial T_0 state multiplicity.

absorption ESR line. Finally, we note that for a negative hyperfine splitting ($A < 0$), it is straightforward to show that opposite polarization would transpire.

Radicals b are also predicted to acquire both α and β electron spin polarization depending on the nuclear spin state of radical a in the radical pair. However, since the ESR spectrum of radical b is a single line, the multiplet CIDEP cancels.

3.3. Polarization quenching

The process of relaxation by the exchange interaction (i.e. Heisenberg spin exchange) may also be visualized by the present vector model. The model does not totally account for relaxation since we have not considered the T_+ and T_- radical pair states. Although these states are unimportant to high-field CIDEP [2], they are very much involved in relaxation by the exchange interaction [5]. We therefore refer to the present account of relaxation as polarization quenching as defined by Pedersen and Freed [6].

Polarization quenching may be viewed by starting with either fig. 2d or 3d and considering J interactions and encounter times, τ_c, that rotate the spin vectors by a distribution of angles greater than 360° (i.e. $|J\tau_c| > 360°$). If the distribution of angles is large enough, the spin vectors will be randomized so that the net components of each radical along the vertical polarization axis are destroyed. Naturally, there is a whole distribution of $J\tau_c$ values in a real system and as a result, polarization by CIDEP and relaxation by Heisenberg spin exchange usually occur simultaneously, with weak exchange interactions (i.e. $J\tau_c \lesssim 1$) contributing to CIDEP and strong exchange ($J\tau_c > 1$) leading to relaxation. It is important to realize, however, that only reencounters of previously paired radicals can result in CIDEP, whereas *any* encounter of radicals can lead to relaxation.

4. Conclusion

A vector model has been presented to provide a simple way of visualizing the process of radical pair CIDEP. The qualitative features of net and multiplet effects are illustrated including the reversals in polarization that are predicted when the initial radical pair multiplicity is changed or when any of the quantities,