Appl. Magn. Reson. 23, 211–233 (2002)

Applied Magnetic Resonance

Vector Model of Electron Spin Echo Envelope Modulation Due to Nuclear Hyperfine and Zeeman Interactions

A. G. Maryasov[1], M. K. Bowman[2], and Y. D. Tsvetkov[1]

[1] Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk, Russian Federation
[2] W.R. Wiley Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory Richland, Washington, USA

Received September 10, 2002; revised September 20, 2002

Abstract. The transverse electron spin magnetization of a paramagnetic center with effective spin $S = 1/2$ interacting with nonquadrupolar nuclei may be presented as a function of pairs of nuclei magnetization vectors which precess around the effective magnetic field directions. Each vector of the pair starts its precession perpendicular to both effective fields. The free induction decay (FID) signal is proportional to the scalar product of the vectors for nuclear spin $I = 1/2$. The electron spin echo (ESE) signal can be described with two pairs of magnetization vectors. The ESE shape is not equal to two back-to-back FID signals except in the absence of ESE envelope modulation. A recursion relation is obtained which allows calculation of ESE signals for larger nuclear spins in the absence of nuclear quadrupole interaction. This relation can be used to calculate the time course of the ESE signal for arbitrary nuclear spin as a function of the nuclear magnetization vectors. Although this formalism allows quantitative calculation of modulation from nuclei, it also provides a qualitative means of visualizing the modulation based on simple magnetization vectors.

1 Introduction

The method of electron spin echo (ESE) spectroscopy [1] is quite effective for determining the structure of paramagnetic centers (PCs) and for studying nuclei immediately surrounding the PC. The spin echo signal provides information on the electron-nuclear hyperfine interaction through the periodic modulation of the echo intensity known as electron spin echo envelope modulation (ESEEM) [1–4]. This phenomenon makes it possible to determine accurate magnetic resonance parameters that can be used to draw valid conclusions about its physical and electronic structure.

In the field of magnetic resonance we usually deal with spaces having large number of dimensions. For example, a paramagnetic center with spin S having one nuclei with spin I has $[(2S + 1)(2I + 1)]^2 - 1$ degrees of freedom. The system behavior can be described as the movement of a vector in the multidimensional space. Unfortunately, the high dimensionality results in a complicated description of related phenomena that is difficult to visualize. The most understandable and intuitively clear situation occurs where the observables can be presented as the motion of a few vectors in subspaces having only two or three dimensions. In such cases a "vector model" may be introduced that draws on our intuitive understanding of mechanics and angular momentum in three dimensions. A well-known example of a vector model is the Bloch equations for spin magnetization motion in external magnetic fields [5]. As far as ESEEM is concerned, there are no vector models which quantitatively describe the phenomenon. W. B. Mims and coworkers [6] (see also part 1 of ref. 2) used a vector model as a qualitative description of ESE modulation but it was neither quantitative nor extensible to other pulsed electron paramagnetic resonance (EPR) signals.

In the present paper we describe a quantitative vector model for modulation which appears in both free induction decay (FID) and ESE signals. This model results from an analysis of the time course of the echo signal and the free induction behavior. Polarization operators [7] are used to obtain an analytical expression for the two-pulse ESEEM for a PC having nuclei with arbitrary spins. It is readily extensible to more complex forms of ESEEM such as the stimulated echo and HYSCORE. Polarization operators make it easy to calculate the integrated echo intensity that corresponds more closely to the experimental measurement than does the traditional calculation of the echo peak intensity.

In addition, the polarization operator formalism is readily extendable to high-frequency EPR at low temperatures or to high-spin systems where the high-temperature approximation breaks down and the electron spin states are highly polarized.

2 System Hamiltonian

Let us consider the case of a radical with electron spin $S = 1/2$ that interacts with N nuclei having spins of I_r (r numbers the nuclei, $r = 1, 2, \ldots, N$). The hyperfine interaction (hfi) of each nuclei is characterized by two quantities: the isotropic hfi constant a_r and the anisotropic hfi tensor $\mathbf{T}_r$, $\mathrm{Tr}(\mathbf{T}_r) = 0$ (all parameters of the spin Hamiltonian are assumed to be in the angular frequency units, rad/s). Both hfi parameters can vary widely with respect to the nuclear Zeeman frequency ω_{Ir}. For convenience we will assume the anisotropy of the $\mathbf{g}$ tensor of the unpaired electron to be small so that its spin is quantized along the direction of a large, external magnetic field which defines the z-axes of both the laboratory and the rotating frames. The spin Hamiltonian for the coupled electron and nuclei in the rotating frame for the electron spin in the absence of the microwave (mw) field is

$$\hat{\mathscr{H}}_f = \delta\omega\hat{S}_z + \sum_{r=1}^{N}(a_r\hat{S}_z\hat{I}_{rz} + \hat{S}_z\vec{T}_r\cdot\hat{\vec{I}}_r + \omega_{Ir}\hat{I}_{rz} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r)\,. \tag{1}$$

Here $\delta\omega$ is the difference between the mw carrier frequency ω and the resonance frequency, ω_0, of the electron spin of the PC in question in the absence of any nuclear couplings ($\delta\omega = \omega_0 - \omega$). The vector $\vec{T}_r$ is defined as the z-row of the anisotropic hfi tensor of the r-th nucleus in the laboratory frame, dot denotes the scalar product of the two vectors, and $\mathbf{Q}_r$ is the nuclear quadrupole interaction tensor. The rotating frame for the electron spin is chosen here because the phases of the mw magnetic field during action of the pulses and of electron transverse magnetization are well defined only with respect to this frame.

Let us write the spin Hamiltonian Eq. (1) with electron polarization operators which are defined as [8]

$$\hat{P}_{\pm} = \frac{1}{2}\hat{E} \pm \hat{S}_z \tag{2}$$

with $\hat{E}$ being the identity operator. These operators are also projection operators onto the eigenstates of the electron spin. With the above operators the Hamiltonian Eq. (1) is

$$\begin{aligned} \hat{\mathscr{H}}_f = {} & \hat{P}_+ \left\{ \frac{\delta\omega}{2} + \sum_r \left[\left(\omega_{Ir} + \frac{a_r}{2} \right) \hat{I}_{rz} + \frac{1}{2} (\hat{T}_r \cdot \hat{\vec{I}}_r) + \hat{\vec{I}}_r \mathbf{Q}_r \hat{\vec{I}}_r \right] \right\} \\ & + \hat{P}_- \left\{ -\frac{\delta\omega}{2} + \sum_r \left[\left(\omega_{Ir} - \frac{a_r}{2} \right) \hat{I}_{rz} - \frac{1}{2} (\hat{T}_r \cdot \hat{\vec{I}}_r) + \hat{\vec{I}}_r \mathbf{Q}_r \hat{\vec{I}}_r \right] \right\}. \end{aligned} \tag{3}$$

Equation (3) clearly shows that the system consists of two subensembles which could be characterized by the quantum number of the electron spin. We wish to emphasize that the two terms at the right-hand side of Eq. (3) do commute with each other. Equation (3) is equivalent to the standard high-field approximation for the electron so that the Hamiltonian is block-diagonal with respect to the electron spin quantum number m_S.

We now define quantization axes $z'_{r,\pm}$ for each nuclear spin subensemble along the net hyperfine and zeeman fields as follows:

$$\vec{k}'_{r,\pm} = \frac{1}{\omega_{r,\pm}} \left(\pm\frac{1}{2}T_{rx}, \quad \pm\frac{1}{2}T_{ry}, \quad \omega_{Ir} \pm \frac{1}{2}(a_r + T_{rz}) \right) \tag{4}$$

with
$$\omega_{r,\pm} = \sqrt{\frac{T_{rx}^2 + T_{ry}^2}{4} + \left[\omega_{Ir} \pm \frac{1}{2}(a_r + T_{rz}) \right]^2} \tag{5}$$

and $\vec{k}'_{r,\pm}$ being the unit vectors along the respective $z'_{r,\pm}$ axis for $m_S = +1/2$ or $-1/2$. The rotating frame Hamiltonian then can be reduced to

$$\hat{\mathscr{H}}_f = \hat{P}_+\left[\frac{\delta\omega}{2} + \sum_r(\omega_{r,+}I_{rz'_{r,+}} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r\ )\right] + \hat{P}_-\left[-\frac{\delta\omega}{2} + \sum_r(\omega_{r,-}I_{rz'_{r,-}} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r\ )\right]. \quad (6)$$

Now we can calculate the evolution operator of our system during a free precession period where there is no applied mw magnetic field

$$U_f(t) = \exp(\imath\mathscr{H}_f t) = \exp\left\{\imath t\hat{P}_+\left[\frac{\delta\omega}{2} + \sum_r(\omega_{r,+}I_{rz'_{r,+}} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r\ )\right]\right\}$$
$$\times\exp\left\{\imath t\hat{P}_-\left[-\frac{\delta\omega}{2} + \sum_r(\omega_{r,-}I_{rz'_{r,-}} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r\ )\right]\right\}. \quad (7)$$

The set of polarization operators (2) and the raising and lowering operators $\hat{S}_\pm$ given by

$$\hat{S}_\pm = S_x \pm \imath\hat{S}_y \quad (8)$$

provide a simple and convenient basis set for the density matrix in each electron spin subspace. This set is easier to use as compared with a more traditional one, $\hat{E}$, $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, due to more simple multiplication properties given by $\hat{P}_\alpha\hat{P}_\beta = \delta_{\alpha\beta}\hat{P}_\alpha$, $\hat{S}_\alpha\hat{S}_\beta = (1-\delta_{\alpha\beta})\hat{P}_\alpha$, $\hat{S}_\alpha\hat{P}_\beta = (1-\delta_{\alpha\beta})\hat{S}_\alpha$, $\hat{P}_\alpha\hat{S}_\alpha = \delta_{\alpha\beta}\hat{S}_\alpha$ (α, $\beta = +, -$). Here $\delta_{\alpha\beta}$ is the Kronecker delta.

With the series expansion and properties of polarization operators, one obtains

$$\exp[\hat{P}_\pm\hat{F}\{\hat{\vec{I}}_r\}] = 1 + \sum_{k=1}^{0}\frac{[\hat{P}_\pm\hat{F}\{\hat{\vec{I}}_r\}]^k}{k!} = 1 + \hat{P}_\pm[\exp[\hat{F}\{\hat{\vec{I}}_r\}] - 1], \quad (9)$$

where $\hat{F}$ is any arbitrary function of the nuclear spins operators. Thus one can rewrite Eq. (7) as

$$U_f(t) = \left(\hat{P}_- + \exp\left(\frac{\imath\delta\omega t}{2}\right)\hat{P}_+\hat{K}_+(t)\right)\left(\hat{P}_+ + \exp\left(-\frac{\imath\delta\omega t}{2}\right)\hat{P}_-\hat{K}_-(t)\right)$$
$$= \exp\left(\frac{\imath\delta\omega t}{2}\right)\hat{P}_+\hat{K}_+(t) + \exp\left(-\frac{\imath\delta\omega t}{2}\right)\hat{P}_-\hat{K}_-(t), \quad (10)$$

where nuclear subsystem evolution operators are introduced for each subensemble,

$$\hat{K}_\pm(t) = \exp\left\{\imath t\sum_r(\omega_{r,\pm}\hat{I}_{rz'_{r,\pm}} + \hat{\vec{I}}_r\mathbf{Q}_r\hat{\vec{I}}_r\ )\right\}. \quad (11)$$

These nuclear operators are products of individual operators of each nuclear spin because the operators for different nuclei commute with each other,

$$\hat{K}_{\pm}(t) = \prod_{r} \hat{K}_{r,\pm}(t)\,, \tag{12}$$

$$\hat{K}_{r,\pm}(t) = \exp[\imath t(\omega_{r,\pm}\hat{I}_{rz'_{r,\pm}} + \hat{\vec{I}}_r \mathbf{Q}_r \hat{\vec{I}}_r\ )]\,. \tag{13}$$

The relations (10) and (12) are the mathematical foundation for the ESEEM "product rule".

For convenience we will make some assumptions about the mw pulses in order to simplify discussion of the evolution of the system following them. We will explicitly consider the simplest situation of ideal "hard" pulses where the whole spectrum of every PC is excited and the pulses can be described as delta function pulses with operators

$$\begin{aligned} U_{pn}(\phi_n, \Theta_n) &= \exp[\imath\,\Theta_n(\,\hat{S}_x \cos\phi_n + \hat{S}_y \sin\phi_n)] \\ &= \hat{E}\cos\left(\frac{\Theta_n}{2}\right) + 2\imath(\,\hat{S}_x \cos\phi_n + \hat{S}_y \sin\phi_n)\sin\left(\frac{\Theta_n}{2}\right), \end{aligned} \tag{14}$$

where ϕ_n is the phase on the n-th mw pulse in the rotating frame with respect to the first pulse, that is, we take $\phi_1 = 0$, and Θ_n is the "turning angle" of the electron spin by the n-th mw pulse. The case of narrow band excitation was considered in ref. 9, see also ref. 4 for more sophisticated techniques that are readily incorporated into our formalism. The approach to the semiquantitative analysis of the manifestation of the finite amplitude of mw pulses in ESEEM spectroscopy was suggested in ref. 10.

3 Calculation Scheme

We seek to describe the evolution of the spin system following a number, N_p, of applied mw pulses with the focus on the simple situations $N_p = 1$, 2 or 3 corresponding to the free induction decay (FID), primary ESE and stimulated ESE signals respectively.

The signal measured by a modern pulse EPR spectrometer consists of two parts – the "in-phase" and the "out-of-phase" components of transverse magnetization. Both quantities can be measured simultaneously and are proportional to the electron transverse magnetization V given by

$$V(t) = V_x(t) + \imath V_y(t) = \mathrm{Tr}(\hat{S}_+\rho(t))\,. \tag{15}$$

Here $\rho(t)$ is the density matrix of our system in the rotating frame. The out-of-phase (V_x) and in-phase (V_y) components of the signal are given by the real and imaginary parts of V, respectively. The relation (15) means that the broadband detection system is used. To emulate narrow band detection discussed by Zhidomirov and Salikhov [9], frequency filtering or integration of Eq. (15) may be used [10].

For our purposes, we can describe the evolution of the spin system density matrix in the form

$$\rho(t) = U_f^+(t-\tau_\Sigma)U_{\mathrm{ev},N_p}^+\rho_1 U_{\mathrm{ev},N_p}U_f(t-\tau_\Sigma)\,. \tag{16}$$

Here the superscript plus denotes the Hermitian conjugate of an operator. The evolution operator $U_{\mathrm{ev},N_p} = U_f U_2 \ldots U_f U_{N_p}$ for the time period between the end of the first mw pulse and the end of the last pulse describes free precession between pulses and the action of all pulses except the first one. The quantity τ_Σ is the total time after the first pulse and equals the sum of the time intervals τ_i between pulses numbered $i+1$ and i,

$$\tau_\Sigma = \sum_i^{N_p-1} \tau_i\,, \tag{17}$$

ρ_i is the density matrix immediately after the action of the i-th mw pulse, thus giving for ρ_1

$$\rho_1 = U_{p_1}^+\rho_0 U_{p_1}\,, \tag{18}$$

ρ_0 is the initial density matrix, usually at thermal equilibrium. In the high-temperature approximation

$$\rho_0 \approx -\frac{h\nu_0}{kT\mathrm{Tr}(1)}\hat{S}_z = -M_0\hat{S}_z\,. \tag{19}$$

The substitution of Eqs. (14) and (19) into Eq. (18) supplies us with the system density matrix immediately after the action of the first mw pulse,

$$\rho_1 = M_0[\hat{S}_y\sin\Theta_1 - \hat{S}_z\cos\Theta_1]\,. \tag{20}$$

We note that ρ_1 does not depend upon the state of the subsystem of nuclear spins. The case of partial or selective excitation when ρ_1 is also dependent on the nuclear spin operators will be considered in a separate paper.

The trace at the right-hand side of Eq. (15) allows us to make calculations easier with Eqs. (15) and (16) and the relation Tr(AB) = Tr(BA). One can obtain

$$\begin{aligned} V(t) &= \mathrm{Tr}(\hat{S}_+U_f^+(t')U_{\mathrm{ev},N_p}^+\rho_1 U_{\mathrm{ev},N_p}U_f(t')) \\ &= \mathrm{Tr}(U_f(t')\hat{S}_+U_f^+(t')U_{\mathrm{ev},N_p}^+\rho_1 U_{\mathrm{ev},N_p}) = \mathrm{Tr}(\hat{M}_+(t')\rho_{N_p})\,, \end{aligned} \tag{21}$$

where t' is the time after the last pulse,

$$t' = t - \tau_\Sigma \,, \tag{22}$$

$$\hat{M}_+(t) = U_f(t)\hat{S}_+ U_f^+(t) \,, \tag{23}$$

and
$$\rho_{N_p} = U^+_{\mathrm{ev},N_p} \rho_1 U_{\mathrm{ev},N_p} \,. \tag{24}$$

An important feature is that the operator $\hat{M}_+$ is independent of any previous history of the spin (which is contained in ρ_{N_p}) and needs to be calculated only once for a given spin Hamiltonian. If needed, $\hat{M}_+$ can be integrated over time independently of ρ to correspond to the use of analog integration or low-pass filters in data acquisition, as is typical in ESE measurements. This particular property is more useful for the FID, the stimulated echo and HYSCORE pulse sequences where the observation window is typically fixed relative to the last mw pulse and a single calculation of $\hat{M}_+$ can be used for an entire dataset. In contrast, the measurement window in a two-pulse echo measurement changes with respect to the final pulse in order to track the position of the electron spin echo so that for each point in the dataset a different function of $\hat{M}_+$ is generally required.

After simple algebra making use of Eq. (10) one can obtain from Eq. (23)

$$\hat{M}_+(t) = \hat{S}_+ \exp(\imath\delta\omega t)\hat{K}_+(t)\hat{K}_-^+(t) = \hat{S}_+ \exp(\imath\delta\omega t)\hat{K}_+(t)\hat{K}_-(-t) \,. \tag{25}$$

The electron and nuclear motions during the free precession period are separated. It is useful to introduce the nuclear modulation operator $\hat{N}$,

$$\hat{N}(t) = \hat{K}_+^+(t)\hat{K}_-(t) = \hat{K}_+(-t)\hat{K}_-(t) \,, \tag{26}$$

so that Eq. (25) becomes

$$M_+(t) = \hat{S}_+ \exp(\imath\delta\omega t)\hat{N}(-t) \,. \tag{27}$$

With Eq. (12) one can write the modulation operator of the whole system as a product of modulation operators of individual nuclei,

$$\hat{N}(t) = \prod_r \hat{N}_r(t) \tag{28}$$

with
$$\hat{N}_r(t) = \hat{K}_{r,+}(-t)\hat{K}_{r,-}(t) \,. \tag{29}$$

In the most general case the density matrix of a PC with $S = 1/2$ may be written as

$$\rho(t) = \hat{S}_+\hat{f}_{s+}(t) + \hat{S}_-\hat{f}_{s-}(t) + \hat{P}_+\hat{f}_{p+}(t) + \hat{P}_-\hat{f}_{p-}(t) \,. \tag{30}$$

The operators $\hat{f}_{s\pm}$, $\hat{f}_{p\pm}$ are functions of the nuclear spins and depend on the spin system history. In appendix the dependence of these operators immediately following a number of mw pulses is found. One can write a formal expression for the signal Eq. (21) with Eqs. (24), (27) and (30)

$$\begin{aligned} V(t') &= \mathrm{Tr}[\hat{S}_+ \exp(\imath\delta\omega t')\hat{N}(-t')(\hat{S}_+\hat{f}_{s+}^{N_p} + \hat{S}_-\hat{f}_{s-}^{N_p} + \hat{P}_+\hat{f}_{p+}^{N_p} + \hat{P}_-\hat{f}_{p-}^{N_p})] \\ &= \exp\big(\imath\delta\omega t'\big)\mathrm{Tr}_{\mathrm{nucl}}[\hat{N}(-t')\hat{f}_{s-}^{N_p}]\,, \end{aligned} \tag{31}$$

where subscript "nucl" means that the trace at the right-hand side of Eq. (31) is taken over all nuclei.

The initial values of the operators, $\hat{f}_{q\pm}^{1}$ $(q = p,\ s)$, can be found with Eq. (20) and Eq. (A2) from appendix

$$\begin{aligned} \hat{f}_{s+}^{1} &= -\frac{\imath}{2}M_0 \sin\Theta_1, \qquad & \hat{f}_{s-}^{1} &= \frac{\imath}{2}M_0 \sin\Theta_1, \\ \hat{f}_{p+}^{1} &= -\frac{1}{2}M_0 \cos\Theta_1, \qquad & \hat{f}_{p-}^{1} &= \frac{1}{2}M_0 \cos\Theta_1. \end{aligned} \tag{32}$$

In the hard-pulse limit, these are scalar functions because the density matrix does not depend on the nuclear spin operators.

The second term in Eq. (20), proportional to the operator $\hat{S}_z$, produces an FID-like signal after a second pulse or additional echoes after a third pulse. Such signals are unwanted when the focus, as in this paper, is on the primary or the stimulated echo in two- or three-pulse sequences. The unwanted signals generally are removed by means of phase cycling and so we truncate Eq. (32) to consider only those signals arising from transverse magnetization during τ_1,

$$\hat{f}_{s\pm}^{1} = \mp\imath\sin\Theta_1, \qquad \hat{f}_{p\pm}^{1} = 0. \tag{33}$$

Now we are prepared to calculate the signal Eq. (31), as a function of the number of applied pulses in the final form. First, we want to summarize our results so far. In Eq. (21), $V(t) = \mathrm{Tr}(\hat{M}_+(t')\rho_{N_p})$, is the detected signal, $\hat{M}_+(t')$ is a function only of the spin Hamiltonian and the time following the final pulse while ρ_{N_p} is the spin density operator at the end of the final pulse and does not evolve during the detection period. Consequently in this formalism, the experimental practicalities of detection, such as an integrator window, are separated and can be treated independently of the spin density matrix and its preparation.

4 Free Induction Decay

In the simplest case of $N_p = 1$ the quantity measured is the FID and $t' = t$ in Eq. (31). After substitution of Eq. (33) one can immediately obtain for the normalized signal

$$V_{\mathrm{FID}}(t) = \frac{\imath}{\mathrm{Tr}_{\mathrm{nucl}}(1)} \sin\Theta_1 \exp(\imath\delta\omega t)\mathrm{Tr}_{\mathrm{nucl}}(\hat{N}(-t)) \,. \tag{34}$$

Application of Eq. (28) leads to a "product rule" for the FID signal and merely reflects the fact that the frequency-domain EPR spectrum is the convolution of the hyperfine structure from each of the nuclei. As expected, the Fourier transform of this FID is the EPR spectrum of the system in the frequency domain.

The modulation operator is easily calculated in a final form in the special case of $I_r = 1/2$ for all interacting nuclei r. In this situation the quadrupole interaction is absent so that Eq. (13) becomes

$$\hat{K}_{r,\pm}(t) = \cos\left(\frac{\omega_{r,\pm} t}{2}\right) + 2\imath \vec{k}'_{r,\pm} \cdot \hat{\vec{I}}_r \sin\left(\frac{\omega_{r,\pm} t}{2}\right). \tag{35}$$

The scalar (dot) product at the right-hand side gives $\vec{k}'_{r,\pm} \cdot \hat{\vec{I}}_r \equiv \hat{I}_{rz'_{r,\pm}}$. After simple algebra (the equation (XIII.83) from ref. 11 was also used in the form $(\vec{q}_1 \cdot \hat{\vec{I}})(\vec{q}_2 \cdot \hat{\vec{I}}) = (1/4)\vec{q}_1 \cdot \vec{q}_2 + (\imath/2)(\vec{q}_1 \otimes \vec{q}_2) \cdot \hat{\vec{I}}$ here) one can obtain for the modulation operator of the r-th nucleus with spin 1/2,

$$\hat{N}_r(t) = \cos\left(\frac{\omega_{r,+} t}{2}\right)\cos\left(\frac{\omega_{r,-} t}{2}\right) + \vec{k}'_{r,+} \cdot \vec{k}'_{r,-} \sin\left(\frac{\omega_{r,+} t}{2}\right)\sin\left(\frac{\omega_{r,-} t}{2}\right) + 2\imath \vec{q}_r(t) \cdot \hat{\vec{I}}_r \,. \tag{36}$$

where
$$\vec{q}_r(t) = \vec{k}'_{r,-} \sin\left(\frac{\omega_{r,-} t}{2}\right)\cos\left(\frac{\omega_{r,+} t}{2}\right) - \vec{k}'_{r,+} \sin\left(\frac{\omega_{r,+} t}{2}\right)\cos\left(\frac{\omega_{r,-} t}{2}\right)$$
$$+ \vec{k}'_{r,+} \otimes \vec{k}'_{r,-} \sin\left(\frac{\omega_{r,+} t}{2}\right)\sin\left(\frac{\omega_{r,-} t}{2}\right). \tag{37}$$

Here symbol $\otimes$ denotes the vector (cross) product of the two vectors. The directions of the effective magnetic fields $\vec{k}'_{r,\pm}$ are given by Eq. (4).

The first two terms in Eq. (36) account for the in-phase electron spin coherence of the form S_+ that appears in the signal while the last term accounts for the antiphase coherence or $S_+ I_z$ in the signal. This antiphase coherence plays an important role in the ESE signal as shown below. Yet, it makes no contribution to the FID signal because it has zero trace, or in other words, because the EPR spectrum is symmetric about its center.

These equations can be rewritten in a more compact form with a pair of auxiliary magnetization vectors $\vec{\mu}'_{r,+}(t)$ defined as follows,

$$\vec{\mu}_{r,\pm}(t) = \vec{k}_r \cos\left(\frac{\omega_{r,\pm} t}{2}\right) + \vec{m}'_{r,\pm} \sin\left(\frac{\omega_{r,\pm} t}{2}\right), \tag{38}$$

where $\vec{k}_r$ is a unit vector perpendicular to both effective field directions, $\vec{k}'_{r,+}$ and $\vec{k}'_{r,-}$,

$$\vec{k}_r = \frac{\vec{k}'_{r,+} \otimes \vec{k}'_{r,-}}{|\vec{k}'_{r,+} \otimes \vec{k}'_{r,-}|}, \tag{39}$$

and the vector $\vec{m}'_{r,\pm}$ is perpendicular to both $\vec{k}'_{r,\pm}$ and $\vec{k}_r$. These vectors are shown in Fig. 1, along with two sets of orthogonal axes defined by the unit vectors $\{\vec{k}'_{r,\pm}, \vec{m}'_{r,\pm}, \vec{k}_r\}$. The vectors $\vec{\mu}_{r,\pm}(t)$ describe the nuclear magnetizations from the two electron spin subensembles. At the end of the first microwave pulse, both $\vec{\mu}_{r,\pm}(t)$ lie along the direction $\vec{k}_r$ (see Fig. 2) and begin free precession around its own respective effective field directed along $\vec{k}'_{r,\pm}$ but scaled to one half of their real strength. Auxiliary vectors with the same properties appeared in the theory of pulsed ELDOR spectroscopy when the finite amplitude of mw field was taken into account [7].

The vector, $\vec{k}_r$, is undefined when the directions of the effective magnetic fields $\vec{k}'_{r,\pm}$ coincide (Eq. (39)). In that case both vectors $\vec{\mu}_{r,\pm}(t)$ rotate in the same plane and their initial directions coincide but their precession frequencies will generally differ. In such situation the FID signal is modulated by the hyperfine splitting but the modulation of the ESE envelope disappears [3]. When the directions of effective fields do not coincide, $\vec{\mu}_{r,\pm}$ precess in planes that lie at some angle with respect to each other and intersect only along $\vec{k}'_r$. This tilt gives rise to the so-called forbidden spin-flip satellite lines in the EPR spectrum, to additional frequencies in the FID, and to the appearance of ESEEM.

The nuclear magnetization vectors permit Eqs. (36) and (37) to be simplified as

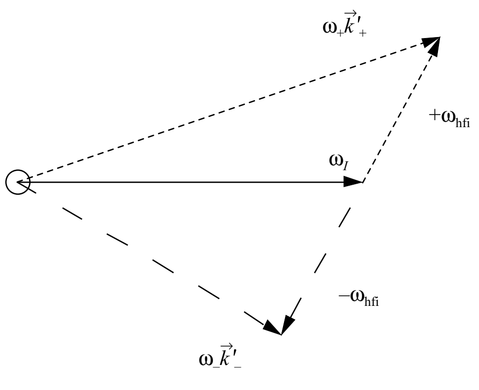

Fig. 1. Effective magnetic fields affecting nuclear spin. The external magnetic field is directed along the Z-axis (marked with ω_I) of the both laboratory and rotating frames. The hyperfine field direction is defined by the orientation of the principle axes of the hfi tensor with respect to the laboratory frame and by the electron quantum number, it is marked with $\pm\omega_{\mathrm{hfi}}$. Vector $\vec{k}$ (see text) is directed perpendicular to the plane of the drawing.

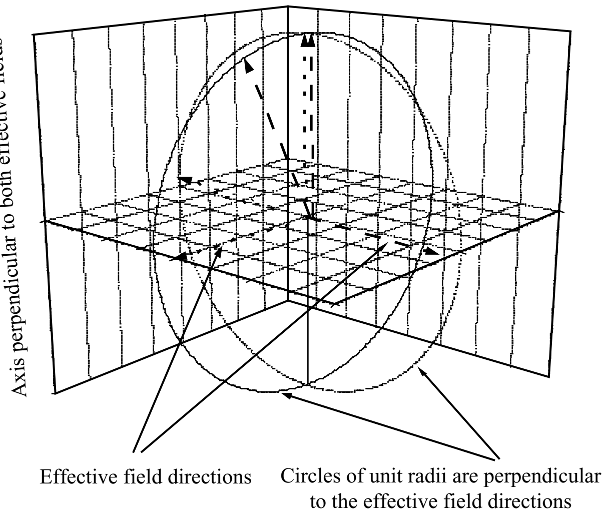

Fig. 2. Vectors of nuclear magnetization in three dimensions. The two vectors of effective magnetic fields (they are marked in the figure) affecting nucleus lie in the horizontal plane. Vertical axis is perpendicular to both effective fields. At the start moment the directions of the nuclear magnetization vectors of unit length coincide (shown in the figure) and are parallel to the vertical axis. Each vector rotates (precesses) in the plane which is perpendicular to the respective effective field, the vector and the effective field are drawn in the same style. Its arrowed end draws a circle on the plane. These circles are also marked in the figure. The vector positions at some nonzero moment of time are also shown.

$$\hat{N}_r(t) = \vec{\mu}_{r,+}(t) \cdot \vec{\mu}_{r,-}(t) + 2\imath\vec{q}_r(t) \cdot \hat{\vec{I}}_r, \tag{40}$$

$$\vec{q}_r(t) = \vec{\mu}_{r,+}(t) \otimes \vec{\mu}_{r,-}(t), \tag{41}$$

making use of the fact that $\vec{k}'_{r,+} \cdot \vec{k}'_{r,-} = \vec{m}'_{r,+} \cdot \vec{m}'_{r,-}$.

Calculation of the FID signal when all nuclei in the system have $I = 1/2$ requires just taking the trace of Eq. (40),

$$V_{\mathrm{FID}}(t) = \imath \sin\Theta_1 \exp(\imath\delta\omega t)\prod_r \vec{\mu}_{r,+}(t) \cdot \vec{\mu}_{r,-}(t) \tag{42}$$

with the relation $\mathrm{Tr}_{\mathrm{nucl}}(\hat{N}(-t)) = \mathrm{Tr}_{\mathrm{nucl}}(\hat{N}(t))$ for nuclear spins of $I = 1/2$.

These results provide a "vector picture" of FID formation in the presence of nuclear spins on the basis of the familiar precession of nuclear spins in their respective effective magnetic fields. The most important feature is that the measured quantity is a scalar product of the vectors whose evolution in time is readily predicted. It is interesting to note that these nuclear magnetization vectors were suggested by Mims [6] to explain qualitatively the ESEEM phenomenon but no quantitative relationships similar to Eqs. (42) or (56) were found.

5 Two-Pulse ESE

Now we consider the primary ESE signal produced by two mw pulses with a time delay τ between them. The relevant operator $\hat{f}^2_{\mathrm{s}-}$ in the spin density operator is derived in appendix in terms of the modulation operator as

$$\hat{f}^2_{s-} = \imath \sin\Theta_1[\exp(\imath\delta\omega\tau) q_2 \hat{N}^{+}(\tau) - \exp(2\imath\phi_2 - \imath\delta\omega\tau) p_2 \hat{N}(\tau)], \tag{43}$$

where the probability, p_i, of an electron spin flip under the action of i-th mw pulse and the complimentary probability, q_i, for the electron spin to retain its projection value are introduced

$$p_i = \sin^2\left(\frac{\Theta_i}{2}\right), \qquad q_i = \cos^2\left(\frac{\Theta_i}{2}\right). \tag{44}$$

The first term in the curly brackets in Eq. (43) leads to a FID-like signal and the second term gives rise to the spin echo. The FID-like signal disappears after averaging over an inhomogeneously broadened EPR spectrum but it can also be eliminated by phase cycling of the second pulse, for example, in the form

$$\begin{aligned}\hat{f}^2_{s-}(\mathrm{ESE}) &= \frac{1}{2}\left\{\hat{f}^2_{s-}(\phi_2 = 0) - \hat{f}^2_{s-}\left(\phi_2 = \frac{\pi}{2}\right)\right\} \\ &= -\imath \sin\Theta_1 p_2 \exp(-\imath\delta\omega\tau)\hat{N}(\tau).\end{aligned} \tag{45}$$

The echo signal has its expected maximum value close to the time 2τ and can be calculated by substitution of Eq. (45) into Eq. (31),

$$V(2\tau + t'') = \frac{-\imath}{\mathrm{Tr}_{\mathrm{nucl}}(1)} \sin\Theta_1 p_2 \exp(\imath\delta\omega t'')\mathrm{Tr}_{\mathrm{nucl}}[\hat{N}(-\tau - t'')\hat{N}(\tau)], \tag{46}$$

where

$$t'' = t - 2\tau. \tag{47}$$

In our limit of delta-function hard pulses, the moment of exact magnetization refocusing occurs at $t = 2\tau$ and the ESE signal is

$$V(2\tau) = \frac{-\imath}{\mathrm{Tr}_{\mathrm{nucl}}(1)} \sin\Theta_1 \sin^2\left(\frac{\Theta_2}{2}\right)\mathrm{Tr}_{\mathrm{nucl}}[\hat{N}(-\tau)\hat{N}(\tau)]. \tag{48}$$

Use of Eq. (28) leads to the product rule for ESEEM [3], and for the time course of the ESE signal

$$V(2\tau + t'') = -\imath V(0)\exp(\imath\delta\omega t'')\prod_{r=1}^{N} V_r(2\tau + t''). \tag{49}$$

Here
$$V_r(2\tau + t'') = \frac{1}{\mathrm{Tr}_{\mathrm{nucl}}(1)} \mathrm{Tr}_{\mathrm{nucl}}[\hat{N}_r(-\tau - t'')\hat{N}_r(\tau)]\,. \tag{50}$$

Equation (49) and the product rule are valid at every point in time after the second microwave pulse in the limit of delta-function mw pulses. However, it is a subtle but important practical point that the use of boxcar integration or most other forms of bandwidth limitation on the ESE signal Eq. (49) during the time t'' leads to violation of the product rule because the integral of a product is not equal to the product of integrals.

This expression can be simplified easily in the case of $I = 1/2$ nuclear spins. After cumbersome algebra one can reduce the operator at the right-hand side of Eq. (50) to

$$\begin{aligned}
&\hat{N}_r(-\tau - t'')\hat{N}_r(\tau) = [\vec{\mu}_{r,+}(-\tau - t'') \cdot \vec{\mu}_{r,-}(-\tau - t'')][\vec{\mu}_{r,+}(\tau) \cdot \vec{\mu}_{r,-}(\tau)] \\
&-[\vec{q}_r(-\tau - t'') \cdot \vec{q}_r(\tau)] + 2\iota\{[\vec{\mu}_{r,+}(-\tau - t'') \cdot \vec{\mu}_{r,-}(-\tau - t'')][\vec{q}_r(\tau) \cdot \hat{\vec{I}}_r] \\
&+[\vec{\mu}_{r,+}(\tau) \cdot \vec{\mu}_{r,-}(\tau)][\vec{q}_r(-\tau - t'') \cdot \hat{\vec{I}}_r] - [\vec{q}_r(-\tau - t'') \otimes \vec{q}_r(\tau)] \cdot \hat{\vec{I}}_r\}\,.
\end{aligned} \tag{51}$$

After substitution of Eq. (37) into Eq. (51) we obtain

$$\begin{aligned}
V_r(2\tau + t'') = {} & [\vec{\mu}_{r,+}(-\tau - t'') \cdot \vec{\mu}_{r,-}(-\tau - t'')][\vec{\mu}_{r,+}(\tau) \cdot \vec{\mu}_{r,-}(\tau)] \\
& -[\vec{\mu}_{r,+}(-\tau - t'') \otimes \vec{\mu}_{r,-}(-\tau - t'')] \cdot [\vec{\mu}_{r,+}(\tau) \otimes \vec{\mu}_{r,-}(\tau)]\,.
\end{aligned} \tag{52}$$

This is a vector picture for the ESE signal on the basis of the same simple nuclear magnetization vectors. But the resulting equation is much more complex than the one for FID, Eq. (42). This additional complexity is due to the antiphase coherence mentioned earlier which appears in the last term of Eq. (52). These vector cross products are difficult to visualize. In addition, there is only partial separation of τ from t''.

Equation (52) forms a starting point for alternate expressions. With Eq. (38) one can rewrite Eq. (52) in terms of the coordinates of the nuclear magnetization vectors. After a long chain of trigonometric transformations the above formula becomes

$$\begin{aligned}
V_r(2\tau + t'') = {} & \cos\left(\frac{\omega_{r,+}t''}{2}\right)\cos\left(\frac{\omega_{r,-}t''}{2}\right) + \cos\beta \sin\left(\frac{\omega_{r,+}t''}{2}\right)\sin\left(\frac{\omega_{r,-}t''}{2}\right) \\
& -2\sin^2\beta \sin\left(\frac{\omega_{r,+}(\tau + t'')}{2}\right)\sin\left(\frac{\omega_{r,-}(\tau + t'')}{2}\right)\sin\left(\frac{\omega_{r,+}\tau}{2}\right)\sin\left(\frac{\omega_{r,-}\tau}{2}\right).
\end{aligned} \tag{53}$$

Here β is the angle between the two effective magnetic fields, Eq. (4), which affect nuclear spin,

$$\cos\beta = \vec{k}'_{r,+}\cdot\vec{k}'_{r,-} = \frac{1}{\omega_{r,+}\omega_{r,-}}\left[\omega_{Ir}^2 - \frac{T_{rx}^2 + T_{ry}^2 + (a_r + T_{rz})^2}{4}\right] \tag{54}$$

and
$$\sin^2\beta = \frac{\omega_{Ir}^2(T_{rx}^2 + T_{ry}^2)}{(\omega_{r,+}\omega_{r,-})^2}. \tag{55}$$

The ESEEM amplitude is proportional to $\sin^2\beta$. This form of the equation easily reduces to the classic expressions of Mims and Zhidomirov and Salikhov for ESEEM when $t'' = 0$. Eq. (52) can be rewritten alternatively as

$$\begin{aligned} V_r(2\tau + t'') &= \vec{\mu}_{r,+}(t'')\cdot\vec{\mu}_{r,-}(t'') \\ &\quad -2[\vec{\mu}_{r\perp,+}(-\tau - t'')\otimes\vec{\mu}_{r\perp,-}(-\tau - t'')]\cdot[\vec{\mu}_{r\perp,+}(\tau)\otimes\vec{\mu}_{r\perp,-}(\tau)], \end{aligned} \tag{56}$$

where
$$\vec{\mu}_{r\perp,\pm}(t) = \vec{m}'_{r,\pm}\sin\left(\frac{\omega_{r,\pm}t}{2}\right). \tag{57}$$

Equation (56) is useful because it clearly shows partial focusing of the electron magnetization at $t'' = 0$ ($t = 2\tau$). It is important to note that Fourier transformation of the ESE signal with respect to time t'' does not reproduce the EPR spectrum in the frequency domain as in the case of the FID. This effect would be predicted on the basis of the results by Zhidomirov and Salikhov[1] [9] and was later demonstrated in two-dimensional (2-D) ESEEM spectra [12]. The difference is caused by the term in Eq. (53) proportional to $\sin^2\beta$ (compare also Eq. (56) with Eq. (42) for the FID). It does not add additional frequencies to the spectrum of the ESE signal but changes the relative intensities of the spectral lines. This term also makes the right-hand side of Eqs. (52), (53) and (56) neither an odd nor an even function of the time t'' thus producing potential asymmetry in the ESE signal. The distortion is proportional to the amplitude of the ESE envelope modulation.

6 Stimulated Echo

When three mw pulses are applied to the system in question, several echoes appear as a response. Only two echoes are of interest here, those produced by

[1] It was shown that the modulation pattern should be different in the cases of broad-band and narrow-band detection of the ESE signal. This proves that the ESE signal is not proportional to two back-to-back FID signals. If the suggestion about the two signals proportionality were true for the system demonstrating the ESE EM effect, the echo signal would be presented as product of the two factors, $V_{\mathrm{ESEEM}}(2\tau + t'') = V_{\mathrm{FID}}(t'')V_{\mathrm{EM}}(2\tau)$. Here $V_{\mathrm{EM}}(2\tau)$ is the well known function describing the modulation pattern. In that case, any manipulation with bandwidth of the receiver at the stage of the signal detection would lead to some transformation of the first factor but could not affect the modulation pattern. The theoretical and experimental results cited prove that the ESE signal cannot be factored in such a manner.

the cumulative action of all mw pulses, namely, the stimulated and the refocused echoes. By exclusion of all FID-like signals and two-pulse echoes one can reduce Eq. (A16) from appendix to

$$\hat{f}^3_{s-} = -\frac{\imath}{4}\sin\Theta_1 \sin\Theta_2 \sin\Theta_3 \exp(-\imath\delta\omega\tau_1)$$
$$\times\{\hat{K}_-(-\tau_2)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1+\tau_2) + \hat{K}_+[-(\tau_1+\tau_2)]\hat{K}_-(\tau_1)\hat{K}_+(\tau_2)$$
$$+\imath\sin\Theta_1 p_2 p_3 \exp[\imath\delta\omega(\tau_1-\tau_2)]\hat{K}_+(-\tau_2)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1)\hat{K}_-(\tau_2), \tag{58}$$

where $\phi_2 = \phi_3 = 0$ is assumed for simplicity. The first term of Eq. (58) is responsible for the appearance of the stimulated echo signal and will be briefly considered below, the second one produces the refocused echo if $\tau_2 > \tau_1$ and otherwise the tail of the "virtual" echo.

In the case of the stimulated echo, $\tau_1 = \tau$ and $\tau_2 = T$. The echo signal appears close to the time $T + 2\tau$. With Eqs. (31) and (58) one can find

$$V_{\mathrm{StESE}}(T+2\tau+t'') = -\frac{\imath}{4\mathrm{Tr}_{\mathrm{nucl}}(1)}\sin\Theta_1 \sin\Theta_2 \sin\Theta_3 \exp(\imath\delta\omega t'')$$
$$\times\mathrm{Tr}_{\mathrm{nucl}}\{\hat{N}(-\tau-t'')[\hat{K}_+(-(\tau+T))\hat{K}_-(\tau)\hat{K}_+(T) + \hat{K}_-(-T)\hat{K}_+(-\tau)\hat{K}_-(\tau+T)]\}, \tag{59}$$

with
$$t'' = t - 2\tau - T. \tag{60}$$

We can present Eq. (59) in the traditional form of the sum of two terms,

$$V_{\mathrm{StESE}}(T+2\tau+t'') = -\frac{\imath}{4}\sin\Theta_1 \sin\Theta_2 \sin\Theta_3 \exp(\imath\delta\omega t'')[V_+ + V_-], \tag{61}$$

where each term may be calculated in accordance with product rule [3],

$$V_\pm = \prod_r V_{r,\pm} \tag{62}$$

with
$$V_{r,\pm} = \frac{1}{\mathrm{Tr}_{\mathrm{nucl}}(1)}\mathrm{Tr}_{\mathrm{nucl}}[\hat{N}_r(-\tau-t'')\hat{K}_{r,\pm}(-T)\hat{N}_r(\tau)\hat{K}_{r,\pm}(T)]. \tag{63}$$

After a long chain of transformations one can obtain

$$V_{r,\pm} = V_r(2\tau+t'') + \sin(\omega_{r,\pm}T)[\vec{q}_r(-\tau-t'')\otimes\vec{q}_r(\tau)]\cdot\vec{k}'_{r,\pm}$$
$$+2\sin^2\left(\frac{\omega_{r,\pm}T}{2}\right)[\vec{q}_r(-\tau-t'')\otimes\vec{k}'_{r,\pm}]\cdot[\vec{q}_r(\tau)\otimes\vec{k}'_{r,\pm}, \tag{64}$$

where the first term describes the primary echo signal and is given, e.g., in Eq. (52). An alternative form is

$$\begin{aligned}V_{r,\pm} &= V_r(2\tau+t'') - \sin(\omega_{r,\pm}T)\left\{\sin\left(\frac{\omega_{r,\mp}(\tau+t'')}{2}\right)\sin\left(\frac{\omega_{r,\mp}\tau}{2}\right)\sin\left(\frac{\omega_{r,\pm}(2\tau+t'')}{2}\right)\right.\\ &\left.+\cos\beta\sin\left(\frac{\omega_{r,\pm}(\tau+t'')}{2}\right)\sin\left(\frac{\omega_{r,\pm}\tau}{2}\right)\sin\left(\frac{\omega_{r,\mp}(2\tau+t'')}{2}\right)\right\}\\ &+2\sin^2\left(\frac{\omega_{r,\mp}T}{2}\right)\left\{\sin\left(\frac{\omega_{r,\pm}(\tau+t'')}{2}\right)\sin\left(\frac{\omega_{r,\mp}(\tau+t'')}{2}\right)\sin\left(\frac{\omega_{r,\pm}\tau}{2}\right)\sin\left(\frac{\omega_{r,\mp}\tau}{2}\right)\right.\\ &\left.-\sin^2\beta\sin\left(\frac{\omega_{r,\mp}(\tau+t'')}{2}\right)\cos\left(\frac{\omega_{r,\pm}(\tau+t'')}{2}\right)\sin\left(\frac{\omega_{r,\mp}\tau}{2}\right)\cos\left(\frac{\omega_{r,\pm}\tau}{2}\right)\right\}. \qquad (65)\end{aligned}$$

The time course of the stimulated echo signal is different from that of the primary ESE. They coincide only when $T = 0$.

7 Recursion Relations for $I > 1/2$ in the Absence of NQI

We can gain considerable insight into the problem of ESEEM from nuclei with large nuclear spin but vanishing quadrupole couplings by considering the question of two equivalent nuclei.

Let us examine a PC that interacts with only two hypothetical equivalent nuclei that have identical hfi and nuclear zeeman interaction but different nuclear spins: one with an arbitrary spin $I_1 > 0$ but the other with $I_2 = 1/2$. The Hamiltonian in this case becomes

$$\begin{aligned}\hat{\mathscr{H}}_{f,\mathrm{eq}} &= \hat{P}_+\left[\frac{\delta\omega}{2} + \left(\omega_I + \frac{a}{2}\right)(\hat{I}_{1z} + \hat{I}_{2z}) + \frac{1}{2}\vec{T}\cdot(\hat{\vec{I}}_1 + \hat{\vec{I}}_2)\right]\\ &+\hat{P}_-\left[-\frac{\delta\omega}{2} + \left(\omega_I - \frac{a}{2}\right)(\hat{I}_{1z} + \hat{I}_{2z}) - \frac{1}{2}\vec{T}\cdot(\hat{\vec{I}}_1 + \hat{\vec{I}}_2)\right]. \qquad (66)\end{aligned}$$

The identical parameters lead to the appearance of an additional constant of motion, the sum of the nuclear spins $\hat{\vec{I}}_\Sigma$,

$$\hat{\vec{I}}_\Sigma = \hat{\vec{I}}_1 + \hat{\vec{I}}_2, \qquad (67)$$

whose square commutes with the Hamiltonian. One can rewrite Eq. (66) in terms of the new quantity,

$$\begin{aligned}\hat{\mathscr{H}}_{f,\mathrm{eq}}(I_\Sigma) &= \hat{P}_+\left[\frac{\delta\omega}{2} + \left(\omega_I + \frac{a}{2}\right)\hat{I}_{\Sigma z} + \frac{1}{2}\vec{T}\cdot\hat{\vec{I}}_\Sigma\right]\\ &+\hat{P}_-\left[-\frac{\delta\omega}{2} + \left(\omega_I - \frac{a}{2}\right)\hat{I}_{\Sigma z} - \frac{1}{2}\vec{T}\cdot\hat{\vec{I}}_\Sigma\right]. \qquad (68)\end{aligned}$$

The total nuclear spin I_Σ cannot change during the time course of a magnetic resonance experiment with this Hamiltonian, so that there is no intersystem crossing in the nuclear subsystem. In the case under consideration $\hat{\vec{I}}_\Sigma$ can have two values, $I_\Sigma = I_1 \pm 1/2$.

The initial equilibrium state of this system may be written to take into account the additional valid quantum number I_Σ. Instead of Eq. (19) we can use

$$\rho_0 \approx -M_0 \hat{S}_z \sum_{I_\Sigma} q(I_1, I_\Sigma) \mid I_\Sigma \rangle\langle I_\Sigma \mid \tag{69}$$

with $|I_\Sigma\rangle\langle I_\Sigma|$ being the projection operator onto the state having the total nuclear spin I_Σ and with

$$q(I_1, I_\Sigma) = \frac{2I_\Sigma + 1}{2(2I_1 + 1)} \tag{70}$$

being the probability to find this system in a state with the total nuclear spin I_Σ.

After repeating the previous calculations for the case of these equivalent nuclei one obtains

$$V(2\tau + t'') = -\imath V(0) \exp(\imath \delta\omega t'') V_{\mathrm{eq}}(2\tau + t'') \tag{71}$$

with the normalized modulation

$$\begin{aligned} V_{\mathrm{eq}}(2\tau + t'') &= \sum_{I_\Sigma} \frac{q(I_1, I_\Sigma)}{2I_\Sigma + 1} \mathrm{Tr}_{\mathrm{nucl}}[\hat{N}_{I_\Sigma}(-\tau - t'')\hat{N}_{I_\Sigma}(\tau)] \\ &= \frac{\mathrm{Tr}_{\mathrm{nucl}}[\hat{N}_{I_1+1/2}(-\tau - t'')\hat{N}_{I_1+1/2}(\tau)] + \mathrm{Tr}_{\mathrm{nucl}}[\hat{N}_{I_1-1/2}(-\tau - t'')\hat{N}_{I_1-1/2}(\tau)]}{2(2I_1 + 1)}. \end{aligned} \tag{72}$$

Equation (26) is still valid for the operator $\hat{N}_{I_\Sigma}$ calculation after the substitution $r \to I_\Sigma$ and

$$\hat{K}_{I_\Sigma \pm}(t) = \exp\left\{ \imath t \left[\left(\omega_I \pm \frac{a}{2} \right) \hat{I}_{\Sigma z} \pm \frac{1}{2} \vec{T} \cdot \hat{\vec{I}}_\Sigma \right] \right\}. \tag{73}$$

Now we can combine the above Eqs. (71) and (72) and the product rules Eqs. (49) and (62) to obtain a relation between the ESEEM signals $V_{[J]}(t)$ belonging to a PC having only the nucleus with spin J,

$$V_{[J]}(t)\ V_{[1/2]}(t) = \frac{J+1}{2J+1} V_{[J+1/2]}(t) + \frac{J}{2J+1} V_{[J-1/2]}(t). \tag{74}$$

This equation produces the following recursion formula

$$V_{[J]}(t) = \frac{4J}{2J+1} V_{[J-1/2]}(t)\, V_{[1/2]}(t) - \frac{2J-1}{2J+1} V_{[J-1]}(t)\,. \tag{75}$$

Here $J \geq 1$, $V_{[0]} = 1$, $V_{[1/2]}(t)$ can be taken from Eqs. (52), (53) and (65). Let us note that Eq. (75) provides additional possibilities for ESEEM calculation as compared with the one developed by Shubin [13, 14] and are closely related to the results by Ponti [15].

Now it is possible to derive a vector picture for the ESE signal for a system with arbitrary nuclear spin I in the absence of NQI with Eq. (75) with the help of either Eq. (52) or Eq. (56).

For example, for $I = 1$ Eq. (75) gives

$$V_{[1]}(t) = \frac{4(V_{[1/2]}(t))^2 - 1}{3}\,, \tag{76}$$

which can be expanded to

$$\begin{aligned} V_{[1]}(2\tau + t'') = {} & \frac{4}{3}\{[\vec{\mu}_{r,+}(t'') \cdot \vec{\mu}_{r,-}(t'')]^2 - 1 \\ & -4[\vec{\mu}_{r,+}(t'') \cdot \vec{\mu}_{r,-}(t'')][\vec{\mu}_{\perp r,+}(-\tau - t'') \otimes \vec{\mu}_{\perp r,-}(-\tau - t'')] \cdot [\vec{\mu}_{\perp r,+}(\tau) \otimes \vec{\mu}_{\perp r,-}(\tau)] \\ & +4\{[\vec{\mu}_{\perp r,+}(-\tau - t'') \otimes \vec{\mu}_{\perp r,-}(-\tau - t'')] \cdot [\vec{\mu}_{\perp r,+}(\tau) \otimes \vec{\mu}_{\perp r,-}(\tau)]\}^2\}\,. \end{aligned} \tag{77}$$

The above equation is more complicated than that for a single $I = 1/2$, but it demonstrates the possibility to represent the ESEEM signal for any nucleus of arbitrary spin in the limit of vanishing quadrupole coupling in terms of the same, simple precessing vectors of nuclear magnetization.

8 Conclusions

A quantitative description of the effects of nuclei with negligible quadrupole couplings on pulsed EPR signals is developed in terms of simple products of vectors moving in a 3-D space. These vectors correspond to nuclear magnetization precessing in the combined effective fields of the external magnet and the hyperfine interaction. There is an effective field for each electron spin projection m_S and the time evolution of the nuclear magnetization vectors is determined only by the precession frequency in each effective field and the angles between the effective fields. The simple vector motion is the same as that described by the classic Bloch equations in the limit of negligible spin relaxation and can be readily visualized. The different experimental pulse sequences produce signals that are vector and scalar products of these simple vectors, however the complexity of the expressions increases rapidly with the number of microwave pulses and the nuclear spin I.

This vector description provides a simple route to the quantitative calculation of ESEEM modulation. In addition, the motion of the vectors is quite simple and allows a qualitatitive visualization of the time course of individual terms and products in the ESEEM equations.

This vector description produces two other important results. The first is the formal result that the pulsed EPR signal is the mathematical trace of the product of two operators. One is the density matrix operator describing the effect of all the microwave pulses and the evolution periods between them. The other operator is the evolution operator for magnetization following the final microwave pulse and is independent of the history of the spin system before that detection period. As a result, it is possible to consider the detection period with any analog integration and filtering independently from the microwave pulses and the variable or swept delays between them that are used to generate the pulsed EPR signal. For the typical stimulated echo or HYSCORE measurement, only a single calculation of the operator for the detection period is necessary.

The other important result is the recursion relation obtained for nuclei with arbitrary spin and no quadrupole interaction. This was obtained from an analysis of hypothetical equivalent nuclei. This recursion relationship allows the use of the same simple nuclear magnetization vectors for all nuclear spins in the limit of negligible quadrupole interaction.

Appendix. Density Matrix as a Function of Pulse Number

Let us assume that we know ρ_i, the density matrix immediately after the action of i-th mw pulse. One can write Eq. (30) in the form

$$\rho_i = \hat{S}_+ \hat{f}^i_{s+} + \hat{S}_- \hat{f}^i_{s-} + \hat{P}_+ \hat{f}^i_{p+} + \hat{P}_- \hat{f}^i_{p-} \,. \tag{A1}$$

The operators, f, can be found easily,

$$\begin{aligned} \hat{f}^i_{s+} &= \mathrm{Tr}_{\mathrm{el}}(\hat{S}_- \rho_i), \qquad & \hat{f}^i_{s-} &= \mathrm{Tr}_{\mathrm{el}}(\hat{S}_+ \rho_i), \\ \hat{f}^i_{p+} &= \mathrm{Tr}_{\mathrm{el}}(\hat{P}_+ \rho_i), \qquad & \hat{f}^i_{p-} &= \mathrm{Tr}_{\mathrm{el}}(\hat{P}_- \rho_i). \end{aligned} \tag{A2}$$

Here the subscript "el" denotes that trace is taken over electron spin variables.

The density matrix after $(i + 1)$-th pulse can be calculated as

$$\rho_{i+1} = U^+_{fp}(\tau_i;\phi_{i+1},\Theta_{i+1})\rho_i U_{fp}(\tau_i;\phi_{i+1},\Theta_{i+1}) \,, \tag{A3}$$

where the evolution operator

$$U_{fp}(\tau_i;\phi_{i+1},\Theta_{i+1}) = U_f(\tau_i) U_{p(i+1)}(\phi_{i+1},\Theta_{i+1}) \tag{A4}$$

describes free motion during time τ_i followed by the $(i + 1)$-th mw pulse. It may be easily found from Eqs. (10) and (14),

$$U_{fp}(\tau;\phi,\Theta) = \cos\left(\frac{\Theta}{2}\right)\left\{\exp\left(\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_+\hat{K}_+(\tau) + \exp\left(-\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_-\hat{K}_-(\tau)\right\}$$
$$+\iota\sin\left(\frac{\Theta}{2}\right)\left\{\exp\left(\frac{\iota\delta\omega\tau}{2} - \iota\phi\right)\hat{S}_+\hat{K}_+(\tau) + \exp\left(\iota\phi - \frac{\iota\delta\omega\tau}{2}\right)\hat{S}_-\hat{K}_-(\tau)\right\}. \qquad \text{(A5)}$$

It is now possible to express the operators $\hat{f}^{i+1}$ in terms of $\hat{f}^{i}$ applying Eq. (A2) with the substitution of $(i + 1)$ for i and using Eqs. (A3) and (A5). The step-by-step calculations are presented below for $\hat{f}^{i+1}_{s+}$ and the final ralations for all the other operators. The indices $(i + 1)$ for ϕ and Θ, and i for τ are omitted for the sake of brevity. At the final stage, the relations $\mathrm{Tr}_{\mathrm{el}}[\hat{S}_\pm] = 0$, $\mathrm{Tr}_{\mathrm{el}}[\hat{P}_\pm] = 1$ were used. The results are:

$$\hat{f}^{i+1}_{s+} = \mathrm{Tr}_{\mathrm{el}}[\hat{S}_-\rho_{i+1}] = \mathrm{Tr}_{\mathrm{el}}\left[\hat{S}_-\left\{\cos\left(\frac{\Theta}{2}\right)\left\{\exp\left(-\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_+\hat{K}_+(-\tau)\right.\right.\right.$$
$$\left.+\exp\left(\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_-\hat{K}_-(-\tau)\right\} - \iota\sin\left(\frac{\Theta}{2}\right)\left\{\exp\left(-\frac{\iota\delta\omega\tau}{2} + \iota\phi\right)\hat{S}_+\hat{K}_+(-\tau)\right.$$
$$\left.\left.\left.+\exp\left(-\iota\phi + \frac{\iota\delta\omega\tau}{2}\right)\hat{S}_+\hat{K}_-(-\tau)\right\}\right\}\rho_i U_{fp}(\tau;\phi,\Theta)\right]$$
$$= \mathrm{Tr}_{\mathrm{el}}\left\{\left[\cos\left(\frac{\Theta}{2}\right)\exp\left(-\frac{\iota\delta\omega\tau}{2}\right)\hat{S}_-\hat{K}_+(-\tau)\right.\right.$$
$$\left.-\iota\sin\left(\frac{\Theta}{2}\right)\exp\left(-\iota\phi + \frac{\iota\delta\omega\tau}{2}\right)\hat{P}_-\hat{K}_-(-\tau)\right]$$
$$\left.\times(\hat{S}_+\hat{f}^i_{s+} + \hat{S}_-\hat{f}^i_{s-} + \hat{P}_+\hat{f}^i_{p+} + \hat{P}_-\hat{f}^i_{p-})U_{fp}(\tau;\phi,\Theta)\right\}$$
$$= \mathrm{Tr}_{\mathrm{el}}\left(\left[\cos\left(\frac{\Theta}{2}\right)\exp\left(-\frac{\iota\delta\omega\tau}{2}\right)[\hat{P}_-\hat{K}_+(-\tau)\hat{f}^i_{s+} + \hat{S}_-\hat{K}_+(-\tau)\hat{f}^i_{p+}]\right.\right.$$
$$\left.-\iota\sin\left(\frac{\Theta}{2}\right)\exp\left(-\iota\phi + \frac{\iota\delta\omega\tau}{2}\right)[\hat{S}_-\hat{K}_-(-\tau)\hat{f}^i_{s-} + \hat{P}_-\hat{K}_-(-\tau)\hat{f}^i_{p-}]\right]$$
$$\times\left\{\cos\left(\frac{\Theta}{2}\right)\left[\exp\left(\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_+\hat{K}_+(\tau) + \exp\left(-\frac{\iota\delta\omega\tau}{2}\right)\hat{P}_-\hat{K}_-(\tau)\right]\right.$$
$$\left.\left.+\iota\sin\left(\frac{\Theta}{2}\right)\left[\exp\left(\frac{\iota\delta\omega\tau}{2} - \iota\phi\right)\hat{S}_+\hat{K}_+(\tau) + \exp\left(\iota\phi - \frac{\iota\delta\omega\tau}{2}\right)\hat{S}_-\hat{K}_-(\tau)\right]\right\}\right)$$
$$= \exp(-\iota\delta\omega\tau)\cos^2\left(\frac{\Theta}{2}\right)\hat{K}_+(-\tau)\hat{f}^i_{s+}\hat{K}_-(\tau) + \exp(\iota\delta\omega\tau - 2\iota\phi)\sin^2\left(\frac{\Theta}{2}\right)$$

$$\times \hat{K}_-(-\tau)\hat{f}^i_{s-}\hat{K}_+(\tau) + \frac{\imath}{2}\exp(-\imath\phi)\sin\Theta$$
$$\times\{\hat{K}_+(-\tau)\hat{f}^i_{p+}\hat{K}_+(\tau) - \hat{K}_-(-\tau)\hat{f}^i_{p-}\hat{K}_-(\tau)\}\,, \tag{A6}$$

$$\hat{f}^{i+1}_{s-} = \exp(\imath\delta\omega\tau)\cos^2\left(\frac{\Theta}{2}\right)\hat{K}_-(-\tau)\hat{f}^i_{s-}\hat{K}_+(\tau) + \exp(2\imath\phi - \imath\delta\omega\tau)\sin^2\left(\frac{\Theta}{2}\right)$$
$$\times \hat{K}_+(-\tau)\hat{f}^i_{s+}\hat{K}_-(\tau) + \frac{\imath}{2}\exp(\imath\phi)\sin\Theta$$
$$\times[\hat{K}_-(-\tau)\hat{f}^i_{p-}\hat{K}_-(\tau) - \hat{K}_+(-\tau)\hat{f}^i_{p+}\hat{K}_+(\tau)]\,, \tag{A7}$$

$$\hat{f}^{i+1}_{p+} = \cos^2\left(\frac{\Theta}{2}\right)\hat{K}_+(-\tau)\hat{f}^i_{p+}\hat{K}_+(\tau) + \sin^2\left(\frac{\Theta}{2}\right)\hat{K}_-(-\tau)\hat{f}^i_{p-}\hat{K}_-(\tau)$$
$$+\frac{\imath}{2}\exp(\imath\phi - \imath\delta\omega\tau)\sin\Theta\hat{K}_+(-\tau)\hat{f}^i_{s+}\hat{K}_-(\tau)$$
$$-\frac{\imath}{2}\exp(-\imath\phi + \imath\delta\omega\tau)\sin\Theta\hat{K}_-(-\tau)\hat{f}^i_{s-}\hat{K}_+(\tau)\,, \tag{A8}$$

$$\hat{f}^{i+1}_{p-} = \cos^2\left(\frac{\Theta}{2}\right)\hat{K}_-(-\tau)\hat{f}^i_{p-}\hat{K}_-(\tau) + \sin^2\left(\frac{\Theta}{2}\right)\hat{K}_+(-\tau)\hat{f}^i_{p+}\hat{K}_+(\tau)$$
$$+\frac{\imath}{2}\exp(\imath\delta\omega\tau - \imath\phi)\sin\Theta\hat{K}_-(-\tau)\hat{f}^i_{s-}\hat{K}_+(\tau)$$
$$-\frac{\imath}{2}\exp(-\imath\delta\omega\tau + \imath\phi)\sin\Theta\hat{K}_+(-\tau)\hat{f}^i_{s+}\hat{K}_-(\tau)\,. \tag{A9}$$

We are interested here in signals resulting from the transverse electron magnetization generated by the first mw pulse. For $N_p = 1$ we retain only terms generating transverse electron magnetization so that

$$\hat{f}^1_{s\pm} = \mp\imath\sin\Theta_1, \qquad \hat{f}^1_{p\pm} = 0. \tag{A10}$$

After application of a second pulse all four terms in Eq. (A1) become potentially relevant so that

$$\hat{f}^2_{s+} = \imath\sin\Theta_1\left[\exp(\imath\delta\omega\tau_1 - 2\imath\phi_2)\sin^2\left(\frac{\Theta_2}{2}\right)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1)\right.$$
$$\left.-\exp(-\imath\delta\omega\tau_1)\cos^2\left(\frac{\Theta_2}{2}\right)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1)\right], \tag{A11}$$

$$\hat{f}^2_{s-} = \imath\sin\Theta_1\left[\exp(\imath\delta\omega\tau_1)\cos^2\left(\frac{\Theta_2}{2}\right)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1)\right.$$
$$\left.-\exp(2\imath\phi_2 - \imath\delta\omega\tau_1)\sin^2\left(\frac{\Theta_2}{2}\right)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1)\right], \tag{A12}$$

$$\hat{f}^2_{p+} = \frac{1}{2}\sin\Theta_1 \sin\Theta_2[\exp(\imath\phi_2 - \imath\delta\omega\tau_1)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1) + \exp(-\imath\phi_2 + \imath\delta\omega\tau_1)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1)], \tag{A13}$$

$$\hat{f}^2_{p-} = -\frac{1}{2}\sin\Theta_1 \sin\Theta_2[\exp(\imath\delta\omega\tau_1 - \imath\phi_2)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1) + \exp(-\imath\delta\omega\tau_1 + \imath\phi_2)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1)]. \tag{A14}$$

In the above formulas we omit terms proportional to $\cos^2(\Theta/2)$ which lead to appearance of unwanted signals. The same equation filtering is applied below.

The operators for the third and subsequent pulses are generated in a straightforward manner.

Acknowledgements

This work was supported by the Russian Basic Research Foundation, Projects 00-15-97321 and 02-03-32022, by NATO Linkage Grant 975194, and by the National Institutes of Health, GM61904. The W.R. Wiley Environmental Molecular Sciences Laboratory is a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

A. G. M. is thankful to Prof. G. M. Zhidomirov for his interest to this work.

The results of this work were presented partly at the VI Voevodsky Conference [16]. The authors are thankful to Profs. G. Gerfen, A. Kawamori, G. Kothe and J. R. Pilbrow for their interest to this work. Special thanks are due to Prof. K. M. Salikhov for the fruitful comments.

References

1. Salikhov K.M., Semenov A.G., Tsvetkov Yu.D.: Electron Spin Echo and Its Applications. Novosibirsk: Nauka 1976.
2. Kevan L. in: Time Domain Electron Spin Resonance (Kevan L., Schwartz R.N., eds.), p. 279. New York: Wiley 1979.
3. Dikanov S.A., Tsvetkov Yu.D.: Electron Spin Echo Envelope Modulation (ESEEM) Spectroscopy. Boca Raton: CRC Press 1992.
4. Schweiger A., Jeschke G.: Principles of Pulse Electron Paramagnetic Resonance. Oxford: University Press 2001.
5. Abragam A.: Principles of Nuclear Magnetism. Oxford: Clarendon Press 1961.
6. Rowan L.G., Hahn E.L., Mims W.B.: Phys. Rev. A **61**, 137 (1965)
7. Maryasov A.G., Tsvetkov Yu.D.: Appl. Magn. Reson. **18**, 583 (2000)
8. Ernst R.R., Bodenhausen G., Wokaun A.: Principles of Nuclear Magnetic Resonance in One and Two Dimensions. Oxford: Clarendon Press 1987.
9. Zhidomirov G.M., Salikhov K.M.: Teor. Eksp. Khim. **4**, 514 (1968)
10. Salikhov K.M., Schneider D.J., Saxena S., Freed J.H.: Chem. Phys. Lett. **262**, 17 (1996)
11. Messiah A.: Quantum Mechanics. Mineola, N.Y.: Dover Publications 1999.

12. Isoya J., Bowman M.K., Norris J.R., Weil J.A.: J. Chem. Phys. **78**, 1735 (1983)
13. Shubin A.A.: Ph.D. Thesis, Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR, 1984.
14. Dikanov S.A., Shubin A.A., Parmon V.N.: J. Magn. Reson. **42**, 474 (1981)
15. Ponti A.: J. Magn. Reson. **127**, 87 (1997)
16. Maryasov A.G., Bowman M.K., Tsvetkov Yu.D. in: Proceedings of the 6th Voevodsky Conference. July 21–25, 2002, Novosibirsk, Russia. p.167, (2002)

Authors' address: Alexander G. Maryasov, Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Ulitsa Institutskaya 3, 630090 Novosibirsk, Russian Federation