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Dynamic Nuclear Polarization in Electron Spin Echo

A. G. Maryasov

Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk, Russian Federation

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Abstract. It is shown that under the action of the proper microwave pulse sequence the equilibrium polarization of the electron spin may be transferred dynamically to the longitudinal nuclear magnetization which will oscillate due to the nuclear spin precession around the effective fields relating to different electron quantum number manifolds. These oscillations may be measured directly in the radio-frequency band. Analytical formulae are obtained for the case when all the nuclei coupled to an unpaired electron have spins of 1/2.

1 Introduction

The pulse electron paramagnetic rezonance (EPR) methods are extensively used for the structure determination of the paramagnetic centers (PCs) containing magnetic nuclei. The electron spin echo (ESE) signal envelope modulation (EM) appeared due to the hyperfine electron nuclear coupling provides information needed for the accurate characterization of the system in question [1–4]. The rather sophisticated pulse sequences are used to produce the echo signal to be analyzed by means of two-dimensional (2-D) Fourier spectroscopy. The general scheme of ESEEM experiment consists of nuclear coherence (NC) generation, mixing and detection [4]. The detection of NC is always performed by means of the electron free induction decay or the ESE signal measurements in the microwave (mw) band [4], for this the NC generated is transferred to the electron transverse magnetization by mw pulses, see, e.g., refs. 5 and 6.

In this contribution the possibility of direct radio-frequency (rf) band measurement of NC generated by mw pulses in the time course of the ESE experiment is predicted.

2 Calculation of Nuclear Coherences

In the most general case the density matrix of a paramagnetic center with $S = 1/2$ may be presented as

$$\rho(t) = \hat{S}_+ \hat{f}_{s+}(t) + \hat{S}_- \hat{f}_{s-}(t) + \hat{P}_+ \hat{f}_{p+}(t) + \hat{P}_- \hat{f}_{p-}(t)\ . \tag{1}$$

Here the set of raising and lowering operators $\hat{S}_\pm$ given by

$$\hat{S}_\pm = \hat{S}_x \pm \imath\, \hat{S}_y \tag{2}$$

and polarization operators [7]

$$\hat{P}_\pm = \frac{1}{2}\hat{E} \pm \hat{S}_z \tag{3}$$

provides with a basis in the electron spin subspace. The operators $\hat{f}_{s\pm}$ and $\hat{f}_{p\pm}$ are functions of nuclear spins coupled to the electron spin and depend on the system history.

In earlier paper devoted to the vector model of ESEEM phenomenon [8], the recurrency relation for the density matrix immediately after the action of the mw pulse sequence was obtained as a function of the number N of short ideal pulses. In accordance with the approach suggested in ref. 8, the signal may be presented in the form

$$\vec{V}(t) = \frac{1}{\mathrm{Tr}(1)} \mathrm{Tr}[\hat{\vec{J}}(t')\rho_N]\,. \tag{4}$$

Here ρ_N is the density matrix immediately after the action of the last (N-th) pulse of the sequence, t' is the time after the last pulse. Three components of nuclear magnetization can be measured separately with appropriately oriented receiver coils, so

$$\hat{\vec{J}}(t) = \beta_n U_f(t)\left(\sum_r g_r \hat{\vec{I}}_r\right) U_f^+(t)\,. \tag{5}$$

Here β_n is the nuclear magneton, index r numbers nuclei coupled to the electron spin, g_r and $\hat{\vec{I}}_r$ are the g factor and vector spin operator of r-th nucleus, respectively, U_f is the system free evolution operator, the superscript plus denotes the Hermitian transposition of the operator, in the case of nonquadrupolar nuclei

$$U_f(t) = \exp(\imath\hat{\mathscr{H}}_f t) = \exp\left[\imath t\hat{P}_+\left(\frac{\omega}{2} + \sum_r \omega_{r,+}\vec{k}'_{r,+}\cdot\hat{\vec{I}}\right)\right]$$
$$\times\exp\left[\imath t\hat{P}_-\left(-\frac{\omega}{2} + \sum_r \omega_{r,-}\vec{k}'_{r,-}\cdot\hat{\vec{I}}\right)\right]. \tag{6}$$

Here the system Hamiltonian $\hat{\mathscr{H}}_f$ is expressed in the units of angular frequency, ω is the resonance frequency of the electron spin, the quantization axis of r-th nucleus for manifolds with electron quantum number $m_s = \pm 1/2$ is given by the unit vector $\vec{k}'_{r,\pm}$

$$\vec{k}'_{r,\pm} = \frac{1}{\omega_{r,\pm}}\left(\pm\frac{1}{2}T_{rx},\ \pm\frac{1}{2}T_{ry},\ \omega_{Ir} \pm \frac{1}{2}(a_r + T_{rz})\right), \tag{7}$$

$\omega_{r,\pm}$ is the strength of the effective magnetic field (in angular frequency units) which is the vector sum of the external magnetic field ω_{Ir} and the hyperfine field produced by the unpaired electron,

$$\omega_{r,\pm} = \left[\frac{T_{rx}^2 + T_{ry}^2}{4} + \left(\omega_{Ir} \pm \frac{1}{2}(a_r + T_{rz})\right)^2\right]^{1/2}, \tag{8}$$

a_r is the hyperfine interaction (hfi) constant and T_{rq} ($q = x, y, z$) are the z-row components of anisotropic part of hfi tensor of the r-th nucleus in the laboratory frame, the dot denotes the scalar product of two vectors.

After substitution of Eq. (6) into Eq. (5) one can obtain

$$\hat{\vec{J}}(t') = \beta_n\left(\hat{P}_+\sum_r g_r[\hat{K}_+(-t')\hat{\vec{I}}_r\hat{K}_+(t')] + \hat{P}_-\sum_r g_r[\hat{K}_-(-t')\hat{\vec{I}}_r\hat{K}_-(t')]\right). \tag{9}$$

Here

$$\hat{K}_\pm(t) = \prod_r \exp(\imath t\omega_{r,\pm}\vec{k}'_{r,\pm}\cdot\hat{\vec{I}}) \tag{10}$$

are nuclear propagators. The trace over the electron spin can be taken easily in Eq. (4) with relation Eq. (9),

$$\vec{V}(t) = \frac{\beta_n}{\mathrm{Tr}_{\mathrm{nucl}}(1)}\mathrm{Tr}_{\mathrm{nucl}}\left(\hat{f}_{p+}^N\sum_r g_r[\hat{K}_+(-t')\hat{\vec{I}}_r\hat{K}_+(t')] + \hat{f}_{p-}^N\sum_r g_r[\hat{K}_-(-t')\hat{\vec{I}}_r\hat{K}_-(t')]\right). \tag{11}$$

Operators $\hat{f}_{p\pm}^N$ are taken immediately after the action of the N-th mw pulse.

For the electron magnetization to be effectively transferred to the nuclear polarization and coherence at least three pulse sequence should be used [5]. Let us consider the NC generator taken from the five-pulse sequence suggested in ref. 5, $(\Theta_1)_x$-τ_1-$(\Theta_2)_{\phi_2}$-τ_2-$(\Theta_3)_{\phi_3}$ it is presented here in a more general form than in the original paper. Here Θ_i is the angle of the electron spin rotation by the i-th mw pulse, ϕ_i is the phase of the i-th pulse in the rotating frame. The final form of operators $\hat{f}_{p\pm}^3$ can be taken from ref. 8. Omitting the terms which will disappear regardless the relation between τ_1 and τ_2 after signal averaging over the inhomogeneous broadening of the EPR spectrum of the PC, one can obtain

$$\begin{aligned}\hat{f}_{p\pm}^3 &= \mp\frac{1}{2}\sin\Theta_1\sin^2\frac{\Theta_2}{2}\sin\Theta_3\\ &\times\{\exp[\imath\delta\omega(\tau_1-\tau_2) - 2\imath\phi_2 + \imath\phi_3]\hat{K}_+(-\tau_2)\hat{K}_-(-\tau_1)\hat{K}_+(\tau_1)\hat{K}_-(\tau_2)\\ &+\exp[2\imath\phi_2 - \imath\phi_3 + \imath\delta\omega(\tau_2-\tau_1)]\hat{K}_-(-\tau_2)\hat{K}_+(-\tau_1)\hat{K}_-(\tau_1)\hat{K}_+(\tau_2)\}\,.\end{aligned} \tag{12}$$

Here $\delta\omega$ is the difference between the carrier frequency of mw pulses and the resonance frequency of the PC. It is clear from Eq. (12) that the third pulse should be applied when the electron transverse magnetization is refocused, thus providing

$$\tau_1 = \tau_2 = \tau. \tag{13}$$

The signal will have the maximum value in the case when

$$\Theta_1 = \Theta_2/2 = \Theta_3 = \pi/2. \tag{14}$$

In a disordered system the only component of the signal Eq. (11) will have a nonzero value, namely, V_z, which is directed along the external magnetic field. Equation (11) may be rewritten with relations Eqs. (12)–(14),

$$\begin{aligned} V_z(t) = \frac{\beta_n}{2\,\mathrm{Tr}_{\mathrm{nucl}}(1)} \sum_r g_r\, \mathrm{Tr}_{\mathrm{nucl}} \{[\hat{G}(\tau)\exp(\iota\varphi) \\ + \hat{G}^{+}(\tau)\exp(-\iota\varphi)][\hat{J}_{rz-}(t') - \hat{J}_{rz+}(t')]\}\,, \end{aligned} \tag{15}$$

where
$$\hat{G}(\tau) = \hat{K}_{+}(-\tau)\hat{K}_{-}(-\tau)\hat{K}_{+}(\tau)\hat{K}_{-}(\tau)\,, \tag{16}$$

$$\varphi = -2\phi_2 + \phi_3\,, \tag{17}$$

$$\hat{J}_{rz\pm}(t) = \hat{K}_{\pm}(-t)\hat{I}_{rz}\hat{K}_{\pm}(t)\,. \tag{18}$$

Each term in Eq. (15) corresponds to free precession of a magnetic moment of the particular nucleus around the respective direction of the effective field (see Eq. (18)), but the initial value of this moment depends also on the state of all other nuclei coupled to the electron spin. This dependence is due to the fact that the electron transverse magnetization is transferred to the NC by the third mw pulse.

The operator $\hat{G}$ can be factorized with Eq. (10),

$$\hat{G}(\tau) = \prod_r \hat{G}_r(\tau)\,, \tag{19}$$

where
$$\hat{G}_r(\tau) = \hat{K}_{r+}(-\tau)\hat{K}_{r-}(-\tau)\hat{K}_{r+}(\tau)\hat{K}_{r-}(\tau) \tag{20}$$

and in the absence of quadrupolar interaction

$$\hat{K}_{r\pm}(t) = \exp(\iota t\omega_{r,\pm}\vec{k}'_{r,\pm}\cdot\hat{\vec{I}})\,. \tag{21}$$

Equation (15) can be rewritten taking account of the possibility to calculate a trace over each nucleus spin separately,

$$V_z(t) = \frac{\beta_n}{2} \sum_r \frac{g_r}{\mathrm{Tr}_r(1)} \mathrm{Tr}_r \{ [\hat{G}_r(\tau) F_r(\tau) \exp(\iota\varphi) + \hat{G}_r^+(\tau) F_r^*(\tau) \exp(-\iota\varphi)][\hat{J}_{rz-}(t') - \hat{J}_{rz+}(t')] \} , \quad (22)$$

where
$$F_r(\tau) = \prod_{n \neq r} \frac{\mathrm{Tr}_n[\hat{G}_n(\tau)]}{\mathrm{Tr}_n(1)} \quad (23)$$

and the superscript asterisk denotes the complex conjugation of the operator.

Let us consider the simplest situation when all nuclei coupled to the unpaired electron of the PC in question have spins of 1/2, $I_r = 1/2$ for all r. In this case

$$\hat{K}_{r,\pm}(t) = \cos\frac{\omega_{r,\pm} t}{2} + 2\iota \vec{k}'_{r,\pm} \cdot \hat{\vec{I}}_r \sin\frac{\omega_{r,\pm} t}{2} . \quad (24)$$

A useful auxiliary operator $\hat{N}'$ may be introduced (compare with the operator $\hat{N}$ in ref. 8),

$$\hat{N}'_r(\tau) = \hat{K}_{r,+}(\tau)\hat{K}_{r,-}(\tau) = \cos\frac{\omega_{r,+}\tau}{2}\cos\frac{\omega_{r,-}\tau}{2} - \cos\beta_r \sin\frac{\omega_{r,+}\tau}{2}\sin\frac{\omega_{r,-}\tau}{2} + 2\iota\vec{Q}_r(\tau)\cdot\hat{\vec{I}}_r . \quad (25)$$

Here β_r is the angle between the two effective fields given in Eq. (7),

$$\cos\beta_r = \vec{k}'_{r,+} \cdot \vec{k}'_{r,-} \quad (26)$$

and
$$\vec{Q}_r(\tau) = \vec{k}'_{r,+} \sin\frac{\omega_{r,+}\tau}{2}\cos\frac{\omega_{r,-}\tau}{2} + \vec{k}'_{r,-} \sin\frac{\omega_{r,-}\tau}{2}\cos\frac{\omega_{r,+}\tau}{2} - \vec{k}'_{r,+} \otimes \vec{k}'_{r,-} \sin\frac{\omega_{r,+}\tau}{2}\sin\frac{\omega_{r,-}\tau}{2} . \quad (24)$$

Here the symbol $\otimes$ is used to denote the cross product of two vectors.

These relations may be simplified with the vector model of ESEEM [8]. Let us introduce two auxiliary nuclear magnetization vectors $\vec{\mu}_{r,\pm}(t)$ defined as follows,

$$\vec{\mu}_{r,\pm}(t) = \vec{k}_r \cos\frac{\omega_{r,\pm} t}{2} + \vec{m}'_{r,\pm} \sin\frac{\omega_{r,\pm} t}{2} , \quad (28)$$

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

$$\vec{k}_r = \frac{\vec{k}'_{r,+} \otimes \vec{k}'_{r,-}}{|\vec{k}'_{r,+} \otimes \vec{k}'_{r,-}|} . \quad (29)$$

The two sets of orthogonal axes are defined by the unit vectors $\{\vec{k}'_{r,\pm}, \vec{m}'_{r,\pm}, \vec{k}_r\}$ where the vector $\vec{m}'_{r,\pm}$ is perpendicular to both $\vec{k}'_{r,\pm}$ and $\vec{k}_r$. The vectors $\vec{\mu}_{r,\pm}(t)$ describe the nuclear magnetizations from the two electron spin subensembles. Each vector precesses around its respective effective magnetic field directed along $\vec{k}'_{r,\pm}$ but scaled to one half of their real strength. With these vectors Eqs. (25) and (27) may written in a more compact form,

$$\hat{N}'_r(\tau) = \vec{\mu}_{r,+}(-\tau) \cdot \vec{\mu}_{r,-}(\tau) + 2\imath \vec{Q}_r(\tau) \cdot \hat{\vec{I}}_r \,, \tag{30}$$

$$\vec{Q}_r(\tau) = \vec{\mu}_{r,+}(-\tau) \otimes \vec{\mu}_{r,-}(\tau) \,. \tag{31}$$

The right-hand side of Eq. (20) may be expressed as a function of operators given in Eq. (30),

$$\hat{G}_r(\tau) = \hat{N}'_r(-\tau)\hat{N}'_r(\tau) \,, \tag{32}$$

thus providing

$$\begin{aligned} \hat{G}_r(\tau) = {} & C_r^2(\tau) - \vec{Q}_r(-\tau) \cdot \vec{Q}_r(\tau) \\ & + 2\imath\{C_r(\tau)[\vec{Q}_r(\tau) + \vec{Q}_r(-\tau)] - \vec{Q}_r(-\tau) \otimes \vec{Q}_r(\tau)\} \cdot \hat{\vec{I}}_r \,. \end{aligned} \tag{33}$$

The scalar product in Eq. (30) is an even function of τ and is denoted as

$$C_r(\tau) = \vec{\mu}_{r,+}(-\tau) \cdot \vec{\mu}_{r,-}(\tau) = C_r(-\tau) \,. \tag{34}$$

Now it is possible to calculate the function F_r defined in Eq. (23) in the final form,

$$F_r(\tau) = \prod_{n \neq r} [C_n^2(\tau) - \vec{Q}_n(-\tau) \cdot \vec{Q}_n(\tau)] \,. \tag{35}$$

The function calculated is real, $F_r^* = F_r$. The main Eq. (22) may be simplified with Eq. (33),

$$\begin{aligned} V_z(t) = \beta_n \sum_r \frac{g_r F_r(\tau)}{\mathrm{Tr}_r(1)} \mathrm{Tr}_r \{ & [\hat{J}_{rz-}(t') - \hat{J}_{rz+}(t')][\cos\varphi [C_r^2(\tau) - \vec{Q}_r(-\tau) \cdot \vec{Q}_r(\tau)] \\ & - 2\sin\varphi\{C_r(\tau)[\vec{Q}_r(\tau) + \vec{Q}_r(-\tau)] - \vec{Q}_r(-\tau) \otimes \vec{Q}_r(\tau)\} \cdot \hat{\vec{I}}_r]\} \,. \end{aligned} \tag{36}$$

The operators $\hat{J}_{rz,\pm}$ describe a precession of the nuclear spin subensembles around the appropriate effective fields and may be easily calculated taking into account that the initial direction of the spin coincides with the z-axis of the laboratory frame (the unit vector along this axis we denote here as $\vec{k}$),

$$\hat{J}_{rz,\pm}(t) = (\vec{k} \cdot \vec{k}'_{r,\pm})(\vec{k}'_{r,\pm} \cdot \hat{\vec{I}}_r) - (\vec{k} \otimes \vec{k}'_{r,\pm}) \cdot \hat{\vec{I}}_r \sin\omega_{r,\pm} t$$

$$+[\hat{I}_{rz} - (\vec{k}\cdot\vec{k}'_{r,\pm})(\vec{k}'_{r,\pm}\cdot\hat{\vec{I}}_r)]\cos\omega_{r,\pm}t\,. \tag{37}$$

The above quantity may be written as a projection of the nuclear spin onto the vector dependent on time with components proportional to the mean value of the nuclear spin in the state with the density matrix given by Eq. (37),

$$\hat{J}_{rz,\pm}(t) = \vec{J}_{r,\pm}(t)\cdot\hat{\vec{I}}_r\,, \tag{38}$$

here

$$\vec{J}_{r,\pm}(t) = (\vec{k}\cdot\vec{k}'_{r,\pm})\,\vec{k}'_{r,\pm} - \vec{k}\otimes\vec{k}'_{r,\pm}\sin\omega_{r,\pm}t + [\vec{k} - (\vec{k}\cdot\vec{k}'_{r,\pm})\vec{k}'_{r,\pm}]\cos\omega_{r,\pm}t\,. \tag{39}$$

With the relation $\mathrm{Tr}[(\vec{a}\cdot\hat{\vec{I}})(\vec{b}\cdot\hat{\vec{I}}) = (\vec{a}\cdot\vec{b})/2$ valid in the case of spin of 1/2 (see note note after Eq. (35)), we can take a trace in Eq. (36),

$$V_z(t) = \beta_n \frac{\sin\varphi}{2}\sum_r g_r F_r(\tau)\{C_r(\tau)[\vec{Q}_r(\tau) + \vec{Q}_r(-\tau)] - \vec{Q}_r(-\tau)\otimes\vec{Q}_r(\tau)\}\cdot[\vec{J}_{r,+}(t') - \vec{J}_{r,-}(t')]. \tag{40}$$

The dynamic polarization of nuclei under the action of mw pulses will be the most effective in the case of

$$\varphi = -2\phi_2 + \phi_3 = \pm\pi/2\,. \tag{41}$$

Let us note that this criterion is fulfilled for the pulse sequence suggested in ref. 5, where $\phi_2 = 0$ and $\phi_3 = -\pi/2$ values were used for the NC generation.

The longitudinal nuclear magnetization given in Eq. (40) may be presented in an alternative (coordinate) form with the relation

$$\vec{k} = \frac{\omega_{r,+}\vec{k}'_{r,+} + \omega_{r,-}\vec{k}'_{r,-}}{2\omega_{Ir}}\,, \tag{42}$$

which immediately follows from the definition (7). After cumbersome algebra

$$\begin{aligned} V_z(t) = \beta_n \frac{\sin\varphi}{4}\sum_r g_r F_r(\tau)\sin^2\beta_r \sin\frac{\omega_{r,+}\tau}{2}\sin\frac{\omega_{r,-}\tau}{2} \\ \times\Bigg[\left(\cos\frac{\omega_{r,+}\tau}{2}\cos\frac{\omega_{r,-}\tau}{2} - \cos\beta\sin\frac{\omega_{r,+}\tau}{2}\sin\frac{\omega_{r,-}\tau}{2}\right) \\ \times\left(\frac{\omega_{r,-}}{\omega_{Ir}}\sin\omega_{r,+}t' + \frac{\omega_{r,+}}{\omega_{Ir}}\sin\omega_{r,-}t'\right) + \frac{\omega_{r,+}}{\omega_{Ir}}\cos\frac{\omega_{r,+}\tau}{2}\sin\frac{\omega_{r,-}\tau}{2}(1-\cos\omega_{r,-}t') \\ + \frac{\omega_{r,-}}{\omega_{Ir}}\sin\frac{\omega_{r,+}\tau}{2}\cos\frac{\omega_{r,-}\tau}{2}(1-\cos\omega_{r,+}t')\Bigg], \end{aligned} \tag{43}$$

We underline here that the longitudinal magnetization Eq. (43) of each nuclei is proportional to the normalized amplitude of modulation of the ESE signal envelope [3, 8], $\sin^2\beta_r$,

$$\sin^2\beta_r = \frac{\omega_{Ir}^2(T_{rx}^2 + T_{ry}^2)}{(\omega_{r,+}\omega_{r,-})^2}. \tag{44}$$

If the time interval between mw pulses is short enough, then

$$\max_r(\omega_{r,\pm}\tau) < 1. \tag{45}$$

Equation (43) may be sufficiently simplified, with the accuracy up to terms of the order of τ^3 one can obtain

$$V_z(t) = \frac{\beta_n\tau^2}{16}\sum_r g_r\omega_{Ir}(T_{rx}^2 + T_{ry}^2) \\ \times\left(\frac{\sin\omega_{r,+}t'}{\omega_{r,+}} + \frac{\sin\omega_{r,-}t'}{\omega_{r,-}} + \frac{\tau}{2}(2 - \cos\omega_{r,-}t' - \cos\omega_{r,+}t')\right). \tag{46}$$

In this case $C_r(\tau) \approx 1$ and a more important relation, $F_r(\tau) \approx 1$, is fulfilled. The latter means that at short time intervals t all the nuclei respond independently of each other. In Eq. (46) the optimal phase value given in Eq. (41) was used. The relative intensity of the signals from nuclei of the different types is proportional to the square of the magnetic moment of nuclei because the nuclear zeeman frequency is defined with the use of the relation $\hbar\omega_{Ir} = g_r\beta_n B_0$ [9], where $\hbar$ is the Planck constant and B_0 is the strength of an external magnetic field.

The spectral density of the nuclear magnetization Eqs. (43) and (45) in disordered system may be obtained as suggested in ref. 10. This will be considered in a separate paper.

It should be noted that the hardware for the longitudinal detection is described in ref. 11 where it was used for the measurements of electron spin-lattice relaxation process.

3 Conclusion

It is shown that spins of nuclei coupled to the spin of an unpaired electron may be dynamically polarized under the action of mw pulses affecting the electron spin. This polarization leads to oscillations of the longitudinal nuclear magnetization which can be detected directly in the rf band. Analytical relations are obtained which describe the predicted effect in the case of arbitrary number of nuclei in the system having spins of 1/2

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