Zeeman Effect of Pure NQR in a Rotating Frame (CW and Pulsed Excitation)*

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The Zeeman effect in a rotating frame is considered for the case when the quadrupolar nuclear spin system is acted on by two radio-frequency fields.

Key words: NQR, Zeeman effect, Radio-frequency field, Rotating frame.

It is known that the spin energy levels of the nuclei ($S > 1/2$) located in an electric field gradient (EFG) are doubly degenerate (integer spins in axially symmetrical EFG and half-integer spins). In an external dc magnetic field the degeneracy of the energy levels is removed (Zeeman effect) [1].

This paper deals with the case of a quadrupolar nuclear spin system which is acted on by two non-parallel radio-frequency (r.f.) fields differing in phase. In the rotating frame (RF) the evolution of the spin system is described by a time-independent effective Hamiltonian [1–3]. The eigenvalues of this Hamiltonian define the energy spectrum of the system. It is shown in the paper that the action upon the quadrupolar nuclear spin system by two r.f. fields leads to the removal of the degeneracy of the system's energy levels in RF (let us call this phenomenon "Zeeman effect in RF").

In the calculation of the energy spectrum of the spin system in RF we restrict ourselves to a single-partial approach. In this case the system's Hamiltonian in the laboratory frame (LF) is

$$H(t) = H_Q + H_1(t)\,, \tag{1}$$

where

$$H_Q = \frac{eQq}{4S(2S-1)}\left\{3S_z^2 - \boldsymbol{S}^2 + \frac{\eta}{2}(S_+^2 + S_-^2)\right\}, \tag{2}$$

$$S_\pm = S_x \pm i S_y\,. \tag{3}$$

eQq and η are the quadrupole interaction constant and the asymmetry parameter. The Hamiltonian $H_1(t)$ describes the interaction of the spin system with linearly-polarised r.f. fields:

$$H_1(t) = \omega_1(\boldsymbol{a}\cdot\boldsymbol{S})\cos(\omega t) + \omega_2(\boldsymbol{b}\cdot\boldsymbol{S})\cos(\omega t + \alpha)\,, \tag{4}$$

where $\omega_1 = \gamma H_1$, $\omega_2 = \gamma H_2$, γ is the gyromagnetic ratio, H_1 and H_2 are the amplitudes of the r.f. fields, $\boldsymbol{a}$ and $\boldsymbol{b}$ are unit vectors parallel to the two fields, given in the principle axes system of the EFG as

$$\boldsymbol{a} = (\sin(\theta_1)\cos(\varphi_1), \sin(\theta_1)\sin(\varphi_1), \cos(\theta_1))\,, \tag{5}$$

$$\boldsymbol{b} = (\sin(\theta_2)\cos(\varphi_2), \sin(\theta_2)\sin(\varphi_2), \cos(\theta_2))\,. \tag{6}$$

Let us consider all spin operators in a basis in which the Hamiltonian H_Q is diagonal. In the projection operators' e_{mn} terms [4], with the matrix elements $\langle m' | e_{mn} | n' \rangle = \delta_{mm'}\,\delta_{nn'}$, the Hamiltonian (1) can be rewritten as

$$H(t) = (2S+1)^{-1} \sum_{mn} \omega_{mn}^0 e_{mm} + \sum_{mn} \{\omega_1(\boldsymbol{a}\cdot\boldsymbol{S})_{mn}\cos(\omega t) + \omega_2(\boldsymbol{b}\cdot\boldsymbol{S})_{mn}\cos(\omega t + \alpha)\}\, e_{mn}\,, \tag{7}$$

where $\omega_{mn}^0 = \lambda_m^0 - \lambda_n^0 = \lambda_{-m}^0 - \lambda_{-n}^0$, λ_m^0 being the eigenvalues of H_Q. Using unitary transformation [2] we can express (7) in RF-representation

$$\tilde{H}(t) = (2S+1)^{-1} \sum_{mn} \Delta_{mn} e_{mm} + \sum_{mn} \{\omega_1(\boldsymbol{a}\cdot\boldsymbol{S})_{mn}\cos(\omega t) + \omega_2(\boldsymbol{b}\cdot\boldsymbol{S})_{mn}\cos(\omega t + \alpha)\}\, e_{mn} \cdot \exp(i\,\omega_{mn} t)\,, \tag{8}$$

where $\Delta_{mn} = \omega_{mn}^0 - \omega$. Taking into account that $\omega_1 \sim \omega_2 \ll |\omega_{mn}^0|$ it is possible to neglect the influence of rapidly oscillating components in (8). As a result,

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the effective Hamiltonian of the system in RF-representation is

$$H_{\text{eff}} = (2S+1)^{-1} \sum_{mn} \Delta_{mn} e_{mm}$$
$$+ \tfrac{1}{2} \sum_{mn} \{[\boldsymbol{S} \cdot (\omega_1 \boldsymbol{a} + \omega_2 \boldsymbol{b} \exp(i\alpha))]_{mn} \delta_{\omega, \omega_{mn}} \tag{9}$$
$$+ [\boldsymbol{S} \cdot (\omega_1 \boldsymbol{a} + \omega_2 \boldsymbol{b} \exp(-\mathrm{i}\alpha))]_{mn} \delta_{\omega, \omega_{nm}}\} e_{mn} .$$

$\delta_{\omega, \omega_{mn}}$ is the Kronecker symbol. Diagonalisation of H_{eff} yields the energy spectrum of the spin system in the RF. As an example, let us consider two important practical cases.

1. $S=1$, $\eta=0$. The quadrupole energy levels for the states $m=\pm 1$ are double degenerate in the LF. The effective Hamiltonian determining the system's energy spectrum in the RF is

$$H_{\text{eff}} = \tfrac{1}{3} \Delta (e_{11} + 2e_{00} + e_{-1-1})$$
$$+ M e_{01} + N e_{-10} + M^* e_{10} + N e_{0-1} , \tag{10}$$

where

$$M = 2^{-3/2}\{(\omega_1 a_1 + \omega_2 b_1 \exp(i\alpha))$$
$$- i(\omega_1 a_2 + \omega_2 b_2 \exp(i\alpha))\} , \tag{11}$$

$$N = 2^{-3/2}\{(\omega_1 a_1 + \omega_2 b_1 \exp(-i\alpha))$$
$$- i(\omega_1 a_2 + \omega_2 b_2 \exp(-i\alpha))\} . \tag{12}$$

Diagonalisation of H_{eff} leads to the next expressions for the energy levels of the system:

$$E_1 = \frac{\Delta}{3} , \tag{13}$$

$$E_{2,3} = -\frac{\Delta}{6} \pm \{\Delta^2 + \omega_1^2 \sin^2(\theta_1) + \omega_2^2 \sin^2(\theta_2) \tag{14}$$
$$+ 2\omega_1 \omega_2 \cos(\alpha) \sin(\theta_1) \sin(\theta_2) \cos(\varphi_1 - \varphi_2)\}^{1/2} .$$

From (13) and (14) it follows that the degeneracy of the energy levels in the RF is removed under the action of only one linearly-polarised field.

2. $S=3/2$, $\eta \neq 0$. The energy levels are doubly degenerate in the LF. In the RF the effective Hamiltonian of the spin system is

$$H_{\text{eff}} = \tfrac{1}{2} \Delta (e_{\frac{3}{2}\frac{3}{2}} - e_{\frac{1}{2}\frac{1}{2}} - e_{-\frac{1}{2}-\frac{1}{2}} + e_{-\frac{3}{2}-\frac{3}{2}}) + R e_{\frac{1}{2}\frac{3}{2}} + R^* e_{\frac{3}{2}\frac{1}{2}}$$
$$+ K e_{-\frac{3}{2}-\frac{1}{2}} + K^* e_{-\frac{1}{2}-\frac{3}{2}} + P(e_{\frac{1}{2}-\frac{3}{2}} - e_{-\frac{1}{2}\frac{3}{2}})$$
$$+ P^*(e_{-\frac{3}{2}-\frac{1}{2}} - e_{\frac{3}{2}-\frac{1}{2}}), \tag{15}$$

where

$$R = G(\omega_1 a_1 + \omega_2 b_1 \exp(i\alpha))$$
$$+ iF(\omega_1 a_2 + \omega_2 b_2 \exp(i\alpha)), \tag{16}$$

$$K = G(\omega_1 a_1 + \omega_2 b_1 \exp(-i\alpha))$$
$$+ iF(\omega_1 a_2 + \omega_2 b_2 \exp(-\mathrm{i}\alpha)), \tag{17}$$

$$P = T(\omega_1 a_3 + \omega_2 b_3 \exp(-i\alpha)), \tag{18}$$

$$G = (\eta+3)/(2\sqrt{3}\xi), \quad F = (\eta-3)/(2\sqrt{3}\xi),$$
$$T = \eta/(\sqrt{3}\xi), \quad \xi = (\eta^2/3+1)^{1/2} . \tag{19}$$

Diagonalisation of the effective Hamiltonian gives us an expression for the energy levels of the spin system in the RF:

$$E_{1,2,3,4} = \pm \left\{\frac{\Delta^2}{4} + \omega_1^2 \boldsymbol{A}^2 + \omega_2^2 \boldsymbol{B}^2 \right. \tag{20}$$
$$\left. + 2\cos(\alpha)(\boldsymbol{A} \cdot \boldsymbol{B})\, \omega_1 \omega_2 \pm 2\sin(\alpha)\, |\boldsymbol{A} \times \boldsymbol{B}|\, \omega_1 \omega_2 \right\}^{1/2} ,$$

where

$$\boldsymbol{A} = (G a_1, F a_2, T a_3), \quad \boldsymbol{B} = (G b_1, F b_2, T b_3), \tag{21}$$

As follows from (20) the degeneracy of energy levels of half integer spins is removed in the RF only under the action of two r.f. fields on each resonance transition.

In the case of pulse excitation (for example MW-4) the spin system's Hamiltonian in RF-representation is

$$H(t) = (2S+1)^{-1} \sum_{mn} \Delta_{mn} e_{mm} \tag{23}$$
$$+ \tfrac{1}{2} f(t) \sum_{mn} \{[\boldsymbol{S} \cdot (\varrho_1 \boldsymbol{a} + \varrho_2 \boldsymbol{b} \exp(i\alpha))]_{mn} \delta_{\omega, \omega_{mn}}$$
$$+ [\boldsymbol{S} \cdot (\varrho_1 \boldsymbol{a} + \varrho_2 \boldsymbol{b} \exp(-i\alpha))]_{mn} \delta_{\omega, \omega_{nm}}\} e_{mn} ,$$

where $f(t) = \sum_{k=0}^{\infty} \delta(t - k t_c - t/2)$, t_c is the multiple-pulse sequence period, $\varrho_1 = \gamma H_1 t_w$, $\varrho_2 = \gamma H_2 t_w$ and t_w is the pulse width. After a transformation which has been used in [2], the effective Hamiltonian of the system is

$$H_{\text{eff}} = \frac{t_w}{2t_c} \sum_{mn} \{[\boldsymbol{S} \cdot (\omega_1 \boldsymbol{a} + \omega_2 \boldsymbol{b} \exp(i\alpha))]_{mn} \delta_{\omega, \omega_{mn}} \tag{24}$$
$$+ [\boldsymbol{S} \cdot (\omega_1 \boldsymbol{a} + \omega_2 \boldsymbol{b} \exp(-i\alpha))]_{mn} \delta_{\omega, \omega_{nm}}\} e_{mn} .$$

In (24) we assumed that $\Delta_{mn}=0$ (resonance case). The effective Hamiltonian denotes the energy spectrum of the spin system in the RF. Diagonalisation of H_{eff} yields the energy levels:

1. $S=1$, $\eta=0$,

$$E_1 = 0, \tag{25}$$

$$E_{2,3} = \pm \frac{t_w}{t_c} \{\omega_1^2 \sin^2(\theta_1) + \omega_2^2 \sin^2(\theta_2)$$
$$+ 2\omega_1 \omega_2 \cos(\alpha) \sin(\theta_1) \sin(\theta_2)$$
$$\cdot \cos(\varphi_1 - \varphi_2)\}^{1/2} . \tag{26}$$

2. $S=3/2,\ \eta \neq 0$,

$$E_{1,2,3,4} = \pm \frac{t_\mathrm{w}}{t_\mathrm{c}} \{\omega_1^2 \boldsymbol{A}^2 + \omega_2^2 \boldsymbol{B}^2 + 2\cos(\alpha)(\boldsymbol{A}\cdot\boldsymbol{B})\,\omega_1\omega_2 \pm 2\sin(\alpha)\,|\boldsymbol{A}\times\boldsymbol{B}|\,\omega_1\omega_2\}^{1/2}. \quad (27)$$

The Zeeman effect in the RF can be used to determine the EFG parameters of crystals. As it has been shown above, the action of r.f. fields removes the energy levels degeneracy of nuclear quadrupole spin systems in the RF. Under the action of an additional alternating magnetic field, the frequency of which is equal to the difference between the energy levels of the system in the RF, it is possible to excite NQR signals in the RF [5]. The direct registration of these signals from single crystals allows to determine the components and orientation of the EFG. Because of the reduction of line broadening effects in the RF [5], the sensitivity of this method is quite high.

In a powder, the spectrum is a superposition of absorption lines originating from all crystallites. From (13), (14) and (20) it follows that the energy levels in all crystallites are different because of the random orientations of the EFG relative to the r.f. magnetic fields. Nevertheless there is a possibility to determine asymmetry parameters in powders. As a example let us consider the $S=3/2$ case when $\omega_1=\omega_2=\omega$, the angle between r.f. fields is $\beta=\pi/2$, $\Delta=0$, and $\alpha=\pi/2$. Then the frequencies of transitions $3\to4$ and $1\to2$ are given by the equations (see (20))

$$\Omega_{3\to4} = 2\omega\{\boldsymbol{A}^2 + \boldsymbol{B}^2 + 2[\boldsymbol{A}^2\boldsymbol{B}^2 - (\boldsymbol{A}\ \boldsymbol{B})^2]^{1/2}\}^{1/2}, \quad (28)$$

$$\Omega_{1\to2} = 2\omega\{\boldsymbol{A}^2 + \boldsymbol{B}^2 - 2[\boldsymbol{A}^2\boldsymbol{B}^2 - (\boldsymbol{A}\ \boldsymbol{B})^2]^{1/2}\}^{1/2}, \quad (29)$$

From the conditions

$$\frac{\partial\Omega}{\partial\cos\theta} = \frac{\partial\Omega}{\partial\varphi} = 0 \quad (30)$$

it is possible to calculate the values of θ and φ defining the resonance frequencies of the transitions $1\to2$ and $3\to4$ for a powder [6]. These frequencies are

$$\Omega_{3\to4} = \omega(6\xi^2)^{-1}\,2\eta, \quad (31)$$

$$\Omega_{1\to2} = \omega(6\xi^2)^{-1}\,6. \quad (32)$$

From the ratio $\Omega_{1\to2}/\Omega_{3\to4}$ the equation for η is obtained as

$$\eta = 3\,\Omega_{3\to4}/\Omega_{1\to2}. \quad (33)$$

The transition frequencies $\Omega_{1\to2}$ and $\Omega_{3\to4}$ are the maxima of absorption of the powder pattern.

The method discussed can be helpful for the investigation of nuclear spin systems with $S>3/2$.

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