

# Bloch-Siegert Effect in Pure Nuclear Quadrupole Resonance\*

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The Bloch-Siegert shift of the NQR frequency is calculated for the case when more than one resonance transition are excited by radiofrequency fields.

**Key words:** NQR, Bloch-Siegert shift, Radiofrequency field.

Bloch and Siegert [1] were the first who showed that the Larmor frequency must have a shift in the presence of the linearly polarized radio frequency (r.f.) field. The Bloch-Siegert shift of the NQR frequency was theoretically studied by Lurcat [2] for the case that the symmetry of the electric field gradient (EFG) is axial and that there is only one resonance transition.

In the present paper the Bloch-Siegert shift of the NQR frequency is considered for the case when more than one quadrupole resonance transition is excited by r.f. fields and EFG symmetry is arbitrary.

Let the nuclear spin system (spin  $S > 1/2$ ) be perturbed by r.f. fields. The behavior of the spin system is described by the equation

$$i d\rho(t)/dt = [H(t), \rho(t)], \quad (1)$$

where  $\rho(t)$  is the density operator,

$$H(t) = H_0 + H_1(t) \quad (2)$$

and

$$H_0 = eQq[4S(2S-1)]^{-1} \cdot [3S_z^2 - S(S+1) + (\eta/2)(S_+^2 + S_-^2)]. \quad (3)$$

$eQq$  and  $\eta$  are the quadrupole-interaction constant and asymmetry parametry of the EFG, respectively.  $H_1(t)$  is the Hamiltonian of the interaction of the spin system with the r.f. fields

$$H_1(t) = \sum_{p=1}^N \gamma H_p S \cos(\omega_p t). \quad (4)$$

Here  $\gamma$  is the gyromagnetic ratio of the nuclei in question and  $H_p$  and  $\omega_p$  are the amplitudes and frequencies of the r.f. fields, respectively.

All the spin operators will be considered in a basis in which the Hamiltonian  $H_0$  is diagonal. We introduce the projection operators  $e_{mn}$  [3], with the matrix elements  $\langle m' | e_{mn} | n' \rangle = \delta_{mm'} \delta_{nn'}$  and express the Hamiltonian (2) in terms of them:

$$H(t) = (2S+1)^{-1} \sum_{mn} \omega_{mn}^0 e_{mn} + \sum_{p=1}^N \sum_{mn} \gamma H_p S_{mn}^p \cos(\omega_p t) e_{mn}. \quad (5)$$

Here  $\omega_{mn}^0 = \lambda_m^0 - \lambda_n^0$ ,  $\lambda_m^0$  are the eigenvalues of  $H_0$ , and  $S_{mn}^p = \langle m | I_p S | n \rangle$ ;  $I_p$  are the unit vectors lying along the r.f. fields  $H_p$ .

After the unitary transformation [4, 5] of (1) the Hamiltonian (5) can be written as

$$\tilde{H}(t) = \sum_{p=1}^N \sum_{mn} \gamma H_p S_{mn}^p \exp(i\omega_{mn}^0 t) \cos(\omega_p t) e_{mn}. \quad (6)$$

The expression (6) can be separated into two parts, a time-independent and a time-dependent term:

$$\tilde{H}(t) = H_0 + H_0(t), \quad (7)$$

where

$$H_0 = \frac{1}{2} \sum_{p=1}^N \sum_{mn} \gamma H_p S_{mn}^p (\delta_{\omega_{mn}^0, \omega_p} + \delta_{\omega_{nm}^0, \omega_p}) e_{mn}, \quad (8)$$

$$H_0(t) = \frac{1}{2} \sum_{p=1}^N \sum_{mn} \gamma H_p \{ S_{nm}^p \exp[i(\omega_{mn}^0 + \omega_p)t] \cdot (1 - \delta_{\omega_{mn}^0, \omega_p}) e_{mn} + S_{mn}^p \exp[-i(\omega_{mn}^0 + \omega_p)t] (1 - \delta_{\omega_{nm}^0, \omega_p}) e_{nm} \}. \quad (9)$$

$\delta_{\omega_{mn}^0, \omega_p}$  is the Kronecker symbol. The expressions (8) and (9) may be considered as a Fourier series of the

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Hamiltonian (7), and using the averaging method [6] we obtain the expression for averaged Hamiltonian accurate to  $\varepsilon^2$  (where  $\varepsilon = (\gamma H_p/eQq) \ll 1$ ):

$$\begin{aligned} \bar{H} = & \frac{1}{2} \sum_{p=1}^N \sum_{mn} \gamma H_p S_{mn}^p (\delta_{\omega_{mn}^0, \omega_p} + \delta_{\omega_{nm}^0, \omega_p}) e_{mn} \\ & + \frac{1}{4} \sum_{p=1}^N \sum_{mn} (\gamma H_p)^2 S_{mn}^p (1 - \delta_{\omega_{mn}^0, \omega_p}) (\omega_{mn}^0 + \omega_p)^{-1} \\ & \cdot [e_{mn}, e_{nm}]. \end{aligned} \quad (10)$$

Using (10) it is easy to find the shift NQR frequencies:

$$\begin{aligned} \omega_{mm'} = & \omega_{mm'}^0 + \sum_{p=1}^N \sum_n (\gamma H_p/2)^2 \\ & \cdot \{ [S_{mn}^p S_{nm}^p + \delta_{\omega_{n-1}^0, 0} (\delta_{n,1} - \delta_{n,-1}) S_{-1n}^p S_{n1}^p] \\ & \cdot [(1 - \delta_{\omega_{nm}^0, \omega_p}) (\omega_{mn}^0 + \omega_p)^{-1} \\ & - (1 - \delta_{\omega_{nm}^0, \omega_p}) (\omega_{nm}^0 + \omega_p)^{-1}] \\ & - [S_{m'n}^p S_{nm'}^p + \delta_{\omega_{n-1}^0, 0} (\delta_{n,1} - \delta_{n,-1}) S_{-1n}^p S_{n1}^p] \\ & \cdot [(1 - \delta_{\omega_{nm}^0, \omega_p}) (\omega_{m'n}^0 + \omega_p)^{-1} \\ & - (1 - \delta_{\omega_{nm}^0, \omega_p}) (\omega_{nm'}^0 + \omega_p)^{-1}] \}. \end{aligned} \quad (11)$$

As an example, we consider particular cases:

1.  $S=1$  and  $\eta=0$ . From (11) it follows

$$\omega_{10} = \omega_0 [1 + \frac{1}{4} (\gamma H_1 \sin \theta / \omega_0)^2], \quad (12)$$

$$\omega_{-10} = \omega_0 [1 + \frac{1}{8} (\gamma H_1 \sin \theta / \omega_0)^2], \quad (13)$$

$$\omega_{1-1} = (\gamma H_1 \sin \theta)^2 / (8 \omega_0). \quad (14)$$

Here  $\omega_0 = 3\pi eQq/2$ .  $\theta$  is the azimuthal angle included between the Z-axis of the EFG and the direction of the r.f. field. In this case the degeneration of the energy level is taken off.

2. For  $S=3/2$  and  $\eta=0$ . The shift NQR frequency is

$$\begin{aligned} \omega_{3/2\ 1/2} = & \omega_0 \{ 1 + (\gamma H_1/16 \omega_0)^2 \\ & \cdot [(2 + 1/\xi) \sin^2 \theta + (1 - 1/\xi^2)(\cos^2 \theta + \sqrt{3} \eta \cos(\varphi)/4)] \}, \end{aligned} \quad (15)$$

where  $\xi = (1 + \eta^2/3)^{1/2}$  and  $\omega_0$  is NQR frequency.

3. For  $S=5/2$  and  $\eta=0$ , when the transitions  $\pm 1/2 - \pm 3/2$  and  $\pm 3/2 - \pm 5/2$  are excited by the r.f. fields  $H_1 \cos(\omega_0 t)$  and  $H_2 \cos(2\omega_0 t)$ , respectively, the shifted frequencies are

$$\begin{aligned} \omega_{3/2\ 1/2} = & \omega_0 + (\gamma H_1 \sin \theta_1)^2 / 12 \omega_0 \\ & - 143 (\gamma H_2 \sin \theta_2) / 192 \omega_0, \end{aligned} \quad (16)$$

$$\begin{aligned} \omega_{5/2\ 3/2} = & 2 \omega_0 + 7 (\gamma H_1 \sin \theta_1)^2 / 12 \omega_0 \\ & + 47 (\gamma H_2 \sin \theta_2) / 96 \omega_0, \end{aligned} \quad (17)$$

$$\begin{aligned} \omega_{5/2\ 1/2} = & 3 \omega_0 - 2 (\gamma H_1 \sin \theta_1)^2 / 3 \omega_0 \\ & + 49 (\gamma H_2 \sin \theta_2) / 192 \omega_0, \end{aligned} \quad (18)$$

where  $\omega_0$  is the NQR frequency of the resonance transition  $\pm 1/2 - \pm 3/2$ .

In particular  $H_2=0$  and  $\theta_1=\pi/2$  it follows from (16) that

$$\omega_{3/2\ 1/2} = \omega_0 + (\gamma H_1)^2 / 12 \omega_0. \quad (19)$$

This result was received early by Lurcat [2].

- [1] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).
- [2] F. Lurcat, J. Phys. Radium **19**, 745 (1958).
- [3] A. R. Kessel, Fiz. Tver. Tela **5**, 1055 (1963).
- [4] N. E. Ainbinder and G. B. Furman, Zh. Eks. Teor. Fiz. **85**, 988 (1983).

- [5] G. B. Furman, Izv. Vuz. Radiofizika **27**, 667 (1984).
- [6] L. L. Buishvili and M. G. Menabde, Zh. Eks. Teor. Fiz. **77**, 2435 (1979).