

# Off-Resonance Nutation NQR Spectroscopy of Powders

N. Ja. Sinjavsky

Department of Physics, Kaliningrad State University, A. Nevsky St. 14, 236041 Kaliningrad, Russia

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The peculiarities of nutation NQR spectra of nuclei with spin  $I=3/2$  in powders are considered in the case of a resonance offset. An equation, which takes into account the offset is given for the determination of the asymmetry  $\eta$ . It is shown that structural of monocystals by means of nutation spectroscopy are possible.

## Introduction

Nuclear quadrupole resonance is one of the most informative methods for the investigation of solids. The possibilities of nutation spectroscopy, however, are little known yet, although such investigations on crystals allow to obtain new information.

For half-integer spins, an asymmetry of the electric field gradient (EFG) tensor at the site of the nucleus does not lead to the disappearance of the degeneracy of the energy levels zero field NQR. Therefore it is not possible to determine the asymmetry parameter and the quadrupole coupling constant  $e^2 Qq$  for spin  $I=3/2$  nuclei (Cl-35, Cl-37, B-11, As-75, Br-79, Br-81) from the single observable NQR frequency. In order to determine the spectral NQR parameters in this case we must switch on a weak magnetic field, and it is necessary to use the Zeeman effect in the case of a monocrystal and of a powder sample as well. This complicates the problem and demands additional equipment. Recently Harbison and Slokenbergs [1, 2] suggested a new two-dimensional nutation NQR experiment which uses the singularities of the nutation spectrum of a powder sample for the determination of the asymmetry parameter  $\eta$ . The calculations of the nutation spectra for  $I=3/2$  and for powders [1, 2] were made without consideration of the spectrometer frequency offset  $\Delta\nu$  of the relative to the Larmor frequency, i.e. the resonance offset. In fact such a frequency deviation always takes place in experiments. As a results of the offset, the experimental nutation spectra become uninterpretable.

Nutation spectra can be obtained by means of an ordinary pulsed NQR Fourier-spectrometer with computer control. The resonance position in the nuta-

tion spectrum for one orientation of a monocrystal with respect to the radio-frequency field  $B_1$  is influenced by the homogeneity of the field  $B_1$ ; therefore one must take a small powder sample for nutation experiments and place it in the centre of the r.f. coil. The simple one-dimensional nutation NQR spectrum is obtained Fourier transforming the free-induction decay  $G(t_w)$  after the radiofrequency excitation pulse, where  $t_w$  is the pulse length, which is increased stepwise in the course of the measuring process.

## Theory and Methods

In order to obtain undistorted nutation spectra, the variable duration of the r.f. pulse must remain smaller than the relaxation times of the sample, i.e.  $t_w \ll T_2^*, T_2, T_1$ . This demands a high power of the transmitter. The field amplitude  $B_1$  must be constant during the  $t_w$  pulse duration, otherwise a false signal arises in the nutation spectrum. This leads to strict requirements for the stability of the power supply the transmitter. In order to excite the spectrum, the offset  $\Delta\nu$  and the r.f. pulse duration must meet the condition  $\Delta\nu t_w \ll 1$ .

A theoretical analysis for spin systems  $I=1$  and  $3/2$  was performed in order to investigate peculiarities of two-dimensional nutation NQR spectra of nitrogen, chlorine and other nuclei in powder and monocrystalline samples. The calculation of the response of the nuclear spin system with electric quadrupole interactions to r.f. pulses with a frequency deviation from resonance is achieved by means of nonstationary perturbation theory with the assumption that the nuclear spin system has no time for the establishment of a new equilibrium in the rotating frame and that, beside, the spin system is insulated from the lattice.

Reprint requests to Prof. Dr. N. Ja. Sinjavsky.

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The intensity of the free induction signals for  $I=3/2$  after an r.f. pulse with width  $t_w$  was obtained in [3] in the form

$$G(t, t_w) = \frac{\alpha}{\xi^2} R^2(\theta, \phi) \sqrt{4\xi^2 \cos^2 \xi t_w + \Delta\omega^2 \sin^2 \xi t_w} \cdot \sin \xi t_w [\omega_0(t - t_w) + \beta], \quad (1)$$

where

$$\alpha = \frac{\gamma B_1}{4}, \quad \xi = \frac{1}{2} \sqrt{4m^2 + \Delta\omega^2}, \quad m = \frac{\alpha R(\theta, \phi)}{\sqrt{3 + \eta^2}},$$

$$R(\theta, \phi) = \sqrt{4\eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6\eta \cos 2\phi)},$$

$$\beta = \arccos\left(\frac{U}{\sqrt{U^2 + V^2}}\right),$$

$$U = \cos \xi t_w \cos \Delta\omega t_w + \frac{\Delta\omega}{2\xi} \sin \xi t_w \sin \Delta\omega t_w,$$

$$V = -\cos \xi t_w \sin \Delta\omega t_w + \frac{\Delta\omega}{2\xi} \sin \xi t_w \cos \Delta\omega t_w.$$

$\theta$  and  $\phi$  represent the orientation of the r.f. field in the principal axis system (PAS) of the EFG tensor.

If a frequency offset is present (as it usually is) the phase of the free induction decay (FID) changes when the r.f. pulse duration  $t_w$  is increased. In order to overcome this problem, all spectra obtained after the first Fourier transformation of  $G(t, t_w)$  (i.e., with respect to  $t$ ) must be phase corrected before the second Fourier transformation, i.e., with respect to  $t_w$ .

The nutation frequency  $2\xi$  depends on the angles  $\theta$  and  $\phi$ . Therefore, in the case of a powder, the powder average must be calculated for these frequencies. The result will be given for the various relative frequency deviations for  $I=1$  and  $I=3/2$  [4].

## Results and Discussion

If  $S(t) = S_0 \sin \omega_0 t$  is the NQR signal at the input of the phase sensitive detector (PSD), and  $A(t) = A_0 \sin(\omega t + \psi)$  is the reference signal, then at the output of the PSD we have the signal  $S_{PSD} \propto S_0 \cos(\Delta\omega t + \psi)$ , where  $\Delta\omega = \omega - \omega_0$  is the offset frequency,  $\omega_0$  is the Larmor frequency, and  $\omega$  denotes the ratio frequency of the spectrometer. For the signal (1) at the output of the phase sensitive detector we have

$$G_{PSD}(t, t_w) \propto \frac{\alpha}{\xi^2} R^2(\theta, \phi) \sin \xi t_w \cdot \sqrt{4\xi^2 \cos^2 \xi t_w + \Delta\omega^2 \sin^2 \xi t_w} \cos [\Delta\omega(t - t_w) - \beta + \psi]. \quad (2)$$

With

$$\cos \beta = \frac{U}{\sqrt{U^2 + V^2}},$$

$$U^2 + V^2 = \frac{1}{4\xi^2} (4\xi^2 \cos^2 \xi t_w + \Delta\omega^2 \sin^2 \xi t_w) \text{ and}$$

$$\cos [\Delta\omega(t - t_w) - \beta + \psi] = \frac{\cos [\Delta\omega(t - t_w) + \psi] U + \sin [\Delta\omega(t - t_w) + \psi] V}{\sqrt{U^2 + V^2}},$$

(2) can be rewritten as

$$G_{PSD}(t, t_w) \propto \frac{2\alpha}{\xi^2} R^2(\theta, \phi) \sin \xi t_w \cdot \{U \cos [\Delta\omega(t - t_w) + \psi] + V \sin [\Delta\omega(t - t_w) + \psi]\}, \quad (3)$$

and then we have

$$G_{PSD}(t, t_w) \propto \frac{2\alpha}{\xi^2} R^2(\theta, \phi) \sin \xi t_w [(U \sin \Delta\omega t_w + V \cos \Delta\omega t_w) \sin (\Delta\omega t + \psi) + (U \cos \Delta\omega t_w + V \sin \Delta\omega t_w) \cos (\Delta\omega t + \psi)]. \quad (4)$$

With

$$\sin \xi t_w (U \sin \Delta\omega t_w + V \cos \Delta\omega t_w) = \frac{\Delta\omega}{4\xi} (1 - \cos 2\xi t_w)$$

and

$$\sin \xi t_w (U \cos \Delta\omega t_w - V \sin \Delta\omega t_w) = \frac{1}{2} \sin 2\xi t_w \quad (5)$$

it follows

$$G_{PSD}(t, t_w) \propto \frac{\alpha}{2\xi^2} R^2(\theta, \phi) [2\xi \sin 2\xi t_w \cos (\Delta\omega t + \psi) - \Delta\omega \cos 2\xi t_w \sin (\Delta\omega t + \psi) + \Delta\omega \sin (\Delta\omega t + \psi)]. \quad (6)$$

The spectrum of a monocrystal contains one nutation frequency  $2\xi$ .

Equation (6) shows that the offset  $\Delta\omega$  leads to the appearance of a zero frequency component in the nutation spectrum. This requires a correction of the constant part in the signal  $G_{PSD}(t, t_w)$ .

We simulated the nutation NQR spectra for  $I=1$  and  $3/2$  by means of the histogram-method. The form of the 2D nutation NQR spectrum for a powder ( $I=3/2$ ,  $\eta \neq 0$ ) with the frequency offset  $\Delta\omega/\gamma B_1 = 0.3$  is shown in Figure 1.

Obviously, a 2D nutation NQR spectrum, which consists of several lines, allows to determine, which lines are caused by inequivalent positions of the EFG tensor axes relative to the radiofrequency field direc-

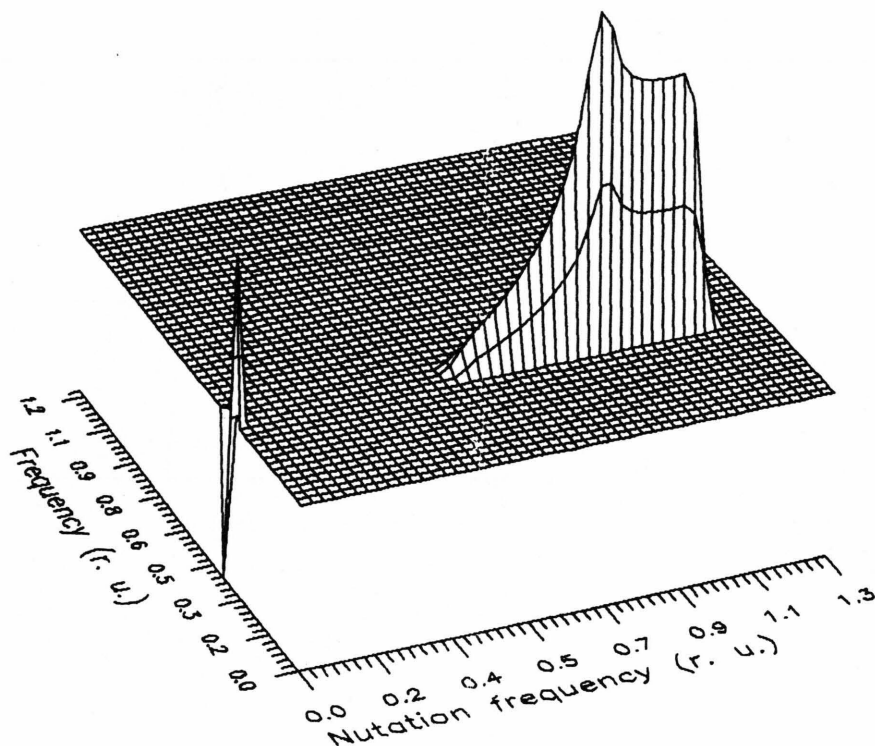


Fig. 1. The simulated off-resonance 2D-nutation NQR spectrum for powder ( $I = 3/2$ ;  $\Delta\omega/\gamma B_1 = 0.3$ ;  $\eta = 0.5$ )

tion, and which lines are caused by various quadrupole interactions. The projection of the 2D nutation spectrum to one of the two axes can be used for the discussion.

The nutation frequency for a monocrystal ( $I = 3/2$ ) is

$$2\xi = \frac{\sqrt{4\alpha^2}}{\sqrt{3+\eta^2}} [4\eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6\eta \cos 2\varphi)] + \Delta\omega^2. \quad (7)$$

We transform (7):

$$\sin^2 \theta = \frac{4 \left[ \frac{(2\xi)^2 - \Delta\omega^2}{(4\alpha)^2} (3 + \eta^2) - \eta^2 \right]}{3(3 - \eta^2 + 2\eta \cos 2\varphi)}. \quad (8)$$

Equation (8) presents a cone with the symmetry axis  $z$ . The nutation frequency for the monocrystal remains constant if the axis of the radio-frequency coils is directed along the conic surface, the parameter of the conic surface depending on the deviation and the asymmetry parameter  $\eta$  of EFG tensor. The equation

of the conic surface for spin  $I = 3/2$  has the form of (8). For spin  $I = 1$  the cones for the second-order frequencies  $\omega_+$  and  $\omega_-$  are imaginary, but it is real for the forbidden transition  $\omega_\Delta = \omega_+ - \omega_-$ :

$$\sin^2 \theta = 1 - \frac{(2\xi)^2 - \Delta\omega^2}{(4\alpha)^2}. \quad (9)$$

An analogous situation for monocrystals in the case of NQR in a constant magnetic field arises when the field is directed along the "zero splitting conic surface" [5, 6]. Then for  $I = 3/2$  in monocrystals instead of four NQR lines only three can be observed [5].

The measurement of the conic surface parameters from the nutation spectrum of a monocrystal allows to determine the asymmetry parameter  $\eta$ . If the radiofrequency field  $B_1$  is directed along the symmetry axis  $z$  of the cone (that is,  $\theta = 0$ ), then

$$\eta = \sqrt{\frac{3(4\xi^2 - \Delta\omega^2)}{16\alpha^2 - 4\xi^2 + \Delta\omega^2}}. \quad (10)$$

Since the number of "conic surfaces" in the crystal is defined by the symmetry class of the crystal [6], the

present method can be used for structure determinations.

The formulas for the NQR-frequencies in the rotating reference frame (RF) for monocrystals and half-integer spins were obtained in [7, 8]. These frequencies are equal to the nutation frequencies. For  $I=3/2$  we have

$$\Omega_{RF} = 2\xi = \sqrt{\Delta\omega^2 + \frac{4\alpha^2}{3+\eta^2} [4\eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6\eta \cos 2\varphi)]} \quad (11)$$

For spin  $I=1$  and for the NQR frequency  $\omega_+$  we obtain

$$\Omega_{RF} = \sqrt{\Delta\omega^2 + (4\alpha)^2 \sin^2 \theta \cos^2 \varphi}. \quad (12)$$

The frequency singularities  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  [1] are obtained as functions of the offset  $\Delta\omega$  in the form

$$\begin{aligned} \omega_1 &= \sqrt{\frac{(4\alpha)^2 \eta^2}{3+\eta^2} + \Delta\omega^2}, \\ \omega_{2,3} &= \sqrt{\frac{4\alpha^2 (3 \mp \eta)^2}{3+\eta^2} + \Delta\omega^2}. \end{aligned} \quad (13)$$

The formula for the experimental determination of the asymmetry parameter from nutation spectra has the form

$$\eta = \frac{3(\sqrt{\omega_3^2 - \Delta\omega^2} - \sqrt{\omega_2^2 - \Delta\omega^2})}{\sqrt{\omega_3^2 - \Delta\omega^2} + \sqrt{\omega_2^2 - \Delta\omega^2}}. \quad (14)$$

In the case of a small frequency deviation  $\Delta\omega \ll 4\alpha$ , instead of (14) a simplified formula is obtained:

$$\eta \approx \frac{3(\omega_3 - \omega_2)}{\omega_3 + \omega_2} \left( 1 + \frac{\Delta\omega^2}{\omega_2 \omega_3} \right). \quad (15)$$

The off-resonance simulated one-dimensional nutation spectrum for powder ( $I=3/2$ ,  $\eta=0.5$ ) without the zero frequency component is present in Figure 2. The nutation frequency is given in relative units ( $2\xi/\gamma B_1$ ); dotted line:  $\Delta\omega/\gamma B_1=0$ , solid line:  $\Delta\omega/\gamma B_1=1$ .

All equations are written for a fixed offset  $\Delta\omega$ . The simulated nutation spectra for powders are obtained by means of the computer with the formal calculation of Gaussian like NQR lines

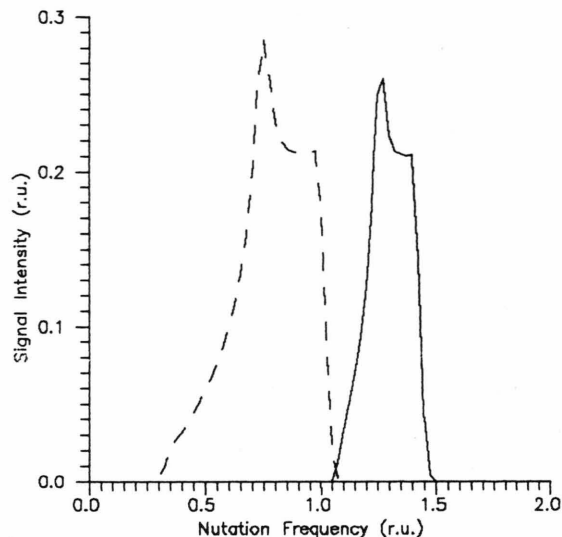


Fig. 2. The dependence of the nutation NQR-spectrum for  $I=3/2$  ( $\eta=0.5$ ) for powder on the frequency deviation:  $\Delta\omega/\gamma B_1=0$  (dotted line) and  $\Delta\omega/\gamma B_1$  (solid line). The nutation frequency is presented in relative units ( $2\xi/\gamma B_1$ ).

The knowledge of nutation NQR frequencies allows a unique solution of the problem of a simultaneous determination of the asymmetry parameter and the quadrupole coupling constant  $e^2 Qq$  not only for  $I=3/2$ , but for any other spin ( $I>1$ ), even if the measurement is carried out only for one quadrupole transition.

In conclusion, the nutation NQR-spectra of powder samples of  $I=3/2$ , nuclei which are measured off-resonance, were interpreted in this work. This is essential for the experimental determination of the parameters  $e^2 Qq$  and  $\eta$  from "pure" NQR data for  $I=3/2$ .

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