PHYSICS OF MAGNETIC PHENOMENA

DETERMINATION OF THE SPECTRAL PARAMETERS OF NUCLEAR QUADRUPOLE RESONANCE FROM NUTATION SPECTRA OF POWDERED SAMPLES

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An analytical expression \( I(\omega) \) is obtained for a normalized function of the shape of an idealized nuclear quadrupole resonance nutation line of a powdered sample for spins \( I = 3/2 \) (\( \eta \neq 0 \)). Calculations are made of the initial moments \( \langle \omega^n \rangle \) of the nutation spectrum of the powder in the form of functions of \( \omega_0 = \gamma B_1 \) and the asymmetry parameter \( \eta \) of the electric field gradient tensor. A method is proposed for determining the spectral parameters \( \eta \) and \( eQq_{zz} \) from the experimentally measured values of \( \langle \omega \rangle \), \( \langle \omega^2 \rangle \), \( \langle \omega^4 \rangle \), and \( \omega_{1/2} \) of the nuclear quadrupole resonance nutation spectrum of the powder.

It is well known that in the case of half-integral nuclear spins, and these are the overwhelming majority except for the nuclei of deuterium \(^2\text{H}\), lithium \(^6\text{Li}\), nitrogen \(^{14}\text{N}\) (\( I = 1 \)), and boron \(^{10}\text{B}\) (\( I = 3 \)), asymmetry of the electric field gradient tensor at an investigated nucleus does not remove the degeneracy of the nuclear quadrupole resonance electric fields in zero field. It is not possible to determine the basic spectral parameters from one experimentally established nuclear quadrupole resonance frequency: neither the quadrupole coupling constant \( eQq_{zz} \) nor the electric field gradient tensor asymmetry parameter \( \eta \). In order to solve the problem for \( I > 3/2 \) it is necessary to measure the nuclear quadrupole resonance frequency of a neighboring transition and, in the case of \( I = 3/2 \), to apply a weak magnetic field to the sample and analyze the Zeeman effect. This greatly complicates the problem for powders and results in a poor accuracy. In the case of single crystals one can determine \( \eta \) using the method of the zero splitting cone [1], but there is more practical interest in powdered samples. In 1989 G. Harbison and A. Slokenberg proposed a two-dimensional experiment with nuclear quadrupole resonance nutation spectroscopy making it possible to utilize a singularity of the nutation spectrum of a powder for nuclei with spin \( I = 3/2 \) in order to determine the asymmetry parameter \( \eta \). The proposed method and the computer modeling of the form of the nutation spectrum are in practice suitable only for exact resonance and large values of the asymmetry parameter. For small values of \( \eta \), the error in determining this parameter from singularities of the nutation spectrum of a powder increases sharply and one is not able to determine an electric field gradient tensor asymmetry parameter of \( \eta < 0.1 \).

The aim of the present work was to obtain an analytical expression for the idealized shape of a nuclear quadrupole resonance nutation spectral line of a powder (\( I = 3/2 \)) and to calculate the statistical characteristics of the distribution of the nutation frequencies for the purposes of utilizing them in order to determine the spectral parameters \( \eta \) and \( eQq_{zz} \) of the nuclear quadrupole resonance line.

The nutation spectrum of a powder takes the form of a superposition of absorption lines in a rotating coordinate system which arise from all the nuclei contained in the large number of randomly orientated single crystals. The integrated intensity of the nutation spectrum in the frequency interval \( \omega_a \) to \( \omega_b \) is proportional to the number of nuclei whose nuclear quadrupole resonance nutation lines fall in this interval. The nuclear quadrupole resonance nutation frequency for spins \( I = 3/2 \) in the presence of detuning from resonance is of the form

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\[ \omega = \left\{ \Delta \omega^2 + \frac{(\gamma B_3)^2}{4(3 + \eta^2)} \left[ 4\eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6\eta \cos 2\phi) \right] \right\}^{1/2}. \] (1)

The integrated intensity \( I(\omega) \) of the nutation spectrum, in a similar way to that of the nuclear magnetic resonance spectrum in a powder [2], will be

\[ \int_0^\omega \int_A^B \sin \theta \, d\theta \, d\phi, \] (2)

where the integration on the right-hand side is taken over the surface (1) between the curves \( \omega = \omega_a \) and \( \omega = \omega_b \). For the particular case \( \eta = 0 \) and \( \Delta \omega \neq 0 \) it follows from Eq. (1) that

\[ \sin \theta = \frac{2\omega'}{\sqrt{3} \gamma B_1}, \quad d\theta = \frac{2d\omega'}{\sqrt{3} (\gamma B_1)^3 - 4\omega'^2}, \quad \omega' = \sqrt{\omega^2 + \Delta \omega^2}, \]

and for an idealized nutation spectrum \( I(\omega) \) of a powder with an axisymmetric electric field gradient tensor in the presence of detuning \( \Delta \omega \neq 0 \) of the frequency from resonance we obtain

\[ I(\omega) = \frac{\omega}{\omega_0 \sqrt{\omega_0^2 - \omega^2}}, \quad 0 < \omega < \omega_0, \] (3)

where \( \omega_0 = \sqrt{\omega_0^2 + \Delta \omega^2} \), \( \omega_0 = \sqrt{3} \gamma B_1/2 \). For \( \eta = 1 \) and \( \Delta \omega = 0 \) we have

\[ I(\omega) = \frac{\omega}{\omega_0 \sqrt{\omega_0^2 - \omega^2}}, \quad \omega > \omega_1, \] (4)

whereupon \( \omega_1 = \omega_2 = \omega_3/2 = \omega_0/\sqrt{3} \).

For the more interesting case \( \eta \neq 0 \) (\( \Delta \omega = 0 \)), following [2] we obtain

\[ \omega^2 = \frac{\omega_0}{3(3 + \eta^2)} \left[ 4\eta^2 x^3 + (1 - x^2) (9 + \eta^2 + 6\eta \cos 2\phi) \right], \quad x = -\cos \theta. \]

Let us find a normalized function of the shape of the nutation line of a powder as

\[ I(\omega) = \frac{2}{\pi} \int_\varphi_1^\varphi_2 \frac{\partial x}{\partial \omega} \, d\phi, \] (5)

where

\[ \frac{\partial x}{\partial \omega} = \frac{3(3 + \eta^2)}{\omega_0^3} \left[ (3\eta^2 - 9 - 6\eta \cos 2\phi) \left\{ \frac{3(3 + \eta^2)}{\omega_0^3} - \frac{3(3 + \eta^2)}{\omega_0^3} \right\} \right]^{-1/2}. \]

Let us introduce the generally adopted notation:

\[ \omega_1 = \frac{2\eta \omega_0}{\sqrt{3(3 + \eta^2)}}, \quad \omega_2 = \frac{(3 - \eta) \omega_0}{\sqrt{3(3 + \eta^2)}}, \quad \omega_3 = \frac{(3 + \eta) \omega_0}{\sqrt{3(3 + \eta^2)}}. \]

Then the integration limits for \( \omega_1 \leq \omega \leq \omega_2 \) are \( \varphi_1 = 0 \) and \( \varphi_2 = \pi/2 \) (case 1) and for \( \omega_2 \leq \omega \leq \omega_3 \) they are

\[ \varphi_1 = \frac{1}{2} \arccos \left\{ \frac{1}{6\eta} \left[ 9 + \eta^2 - \frac{3(3 + \eta^2) \omega_3^2}{\omega_0^3} \right] \right\}, \quad \varphi_2 = \pi/2 \quad \text{(case 2)}. \]