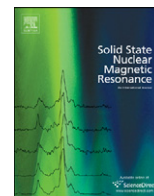




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QUEST—QUadrupolar Exact SoftWare: A fast graphical program for the exact simulation of NMR and NQR spectra for quadrupolar nuclei

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ABSTRACT

We present a new program for the exact simulation of solid-state NMR spectra of quadrupolar nuclei in stationary powdered samples which employs diagonalization of the combined Zeeman-quadrupolar Hamiltonian. The program, which we call QUEST (QUadrupolar Exact SoftWare), can simulate NMR spectra over the full regime of Larmor and quadrupolar frequency ratios, which encompasses scenarios ranging from high-field NMR to nuclear quadrupole resonance (NQR, where the Larmor frequency is zero) and does not make use of approximations when treating the quadrupolar interaction. With the use of the fast powder averaging scheme of Alderman, Solum, and Grant [51], exact NMR spectral simulations are only marginally slower than the second-order perturbation theory counterpart. The program, which uses a graphical user interface, also incorporates chemical shift anisotropy and non-coincident chemical shift and quadrupolar tensor frames. The program is validated against newly-acquired experimental data through several examples including: the low-field $^{79/81}\text{Br}$ NMR spectra of CaBr_2 , the ^{14}N overtone NMR spectrum of glycine, the ^{187}Re NQR spectra of $\text{Re}_2(\text{CO})_{10}$, and lastly the ^{127}I overtone NQR spectrum of SrI_2 , which, to the best of our knowledge, represents the first direct acquisition of an overtone NQR spectrum for a powdered sample.

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1. Introduction

With the advent of higher field persistent magnets and the development of special pulse schemes designed to enhance the sensitivity of solid-state nuclear magnetic resonance (NMR) experiments, nuclei that were once considered highly impractical to study by NMR are now being studied in the context of a wide range of applications [1–12]. This is particularly true for quadrupolar nuclei ($I > 1/2$), which comprise nearly 75% of the stable NMR-active nuclei in the periodic table. Quadrupolar nuclei possess a non-spherical charge distribution which can be quantified by a scalar value known as the nuclear electric quadrupole moment (Q). This moment interacts with the electric field gradient (EFG) generated by the nuclei and electrons around the probe nucleus, resulting in the so-called quadrupolar interaction.

The quadrupolar interaction operates in a molecule- or lattice-based frame, whereas the fundamental Zeeman interaction common to most NMR experiments operates in the lab frame which is imposed by an applied magnetic field. These two interactions have fundamentally different and independent foundations and two forms of nuclear resonance spectroscopy can be employed to study these nuclei. In nuclear quadrupole resonance (NQR), the

quadrupolar interaction is the dominant interaction, while in NMR spectroscopy, the Zeeman interaction is assumed to be dominant. It is well known that when performing magnetic resonance experiments on real samples which possess quadrupolar nuclei, the intermediate region is ill-defined [13–17]. It has been common practice to use perturbation theory to analyze the spectra [18,19], although these methods may not be valid in certain circumstances. As the solid-state NMR community pushes towards the study of nuclei with ever larger quadrupolar interactions (via large- Q nuclei and/or large EFGs) or smaller Zeeman interactions (for low- γ nuclei, where γ is the magnetogyric ratio of the nucleus), perturbation theory treatments for isolated spins may no longer be useful and the use of exact solutions will become necessary in some cases. This has been demonstrated for some ^{127}I , $^{185/187}\text{Re}$, $^{35/37}\text{Cl}$, and ^{27}Al NMR spectra where a second-order perturbation theory model under the high-field approximation was shown to break down [1,2,20–22]. Exact NMR/NQR solutions are also being used to study a wide range of interesting systems [23–25].

To our knowledge, there is no generally available and user-friendly software which treats the Zeeman-quadrupolar Hamiltonian exactly, and includes contributions from chemical shift anisotropy. We have then decided, in conjunction with much of the work being done in our lab [21,26], to design a fast and exact NMR/NQR simulation program with a graphical user interface (GUI) in order to simulate spectra. In this paper, we shall briefly

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recapitulate the relevant theory, describe the user interface of our QUadropolar Exact SoftWare (QUEST), as well as show examples of simulations from NMR, NQR, and NMR/NQR overtone transitions, including the first literature example of the direct acquisition of overtone NQR spectra in a powdered sample.

2. Theory

The total spin Hamiltonian may be represented as a sum of the individual interaction Hamiltonians. In the case of quadrupolar nuclei (and for QUEST), most often only the Zeeman, quadrupolar, and chemical shift interactions are important [18]. Hence, for a diamagnetic sample in the solid state, the relevant total spin Hamiltonian for a quadrupolar nucleus in a magnetic field can be written as follows [14,16]:

$$\hat{H}_{ZQ} = -\nu_0(1 + \delta_{ZZ})\hat{I}_z + \frac{C_Q}{4I(2I-1)} \begin{bmatrix} \frac{1}{3}\sqrt{6}(3\hat{I}_z^2 - \hat{I}^2)V_0 + (\hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z)V_{-1} \\ -(\hat{I}_z\hat{I}_- + \hat{I}_-\hat{I}_z)V_{+1} + \hat{I}_+^2V_{-2} + \hat{I}_-^2V_{+2} \end{bmatrix} \quad (1)$$

where ν_0 is the Larmor frequency and m is the magnetic quantum number which can take values ranging from $+I$ to $-I$. C_Q is the quadrupolar coupling constant which is itself defined as $eV_{33}Q/h$ where e is the fundamental charge, V_{33} is the EFG principal tensor component of largest magnitude, and h is Planck's constant. In general, the principal components of the EFG tensor are ordered as $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. The V_n ($n=0, \pm 1, \pm 2$) terms are spherical tensor components which can be calculated according to Man and Vega [15,16].

$$\begin{aligned} V_0 &= 3\sqrt{1/6}V_{zz} \\ V_{+1} &= -V_{xz} - iV_{yz} \\ V_{-1} &= V_{xz} - iV_{yz} \\ V_{+2} &= \frac{1}{2}(V_{xx} - V_{yy}) + iV_{xy} \\ V_{-2} &= \frac{1}{2}(V_{xx} - V_{yy}) - iV_{xy} \end{aligned} \quad (2)$$

The angular dependence is held in the V_{xx} , V_{xy} type terms. These are written as follows:

$$\begin{aligned} V_{xx} &= \frac{1}{2}(3\sin^2\theta - 1 - \eta\cos^2\theta\cos 2\phi) \\ V_{yy} &= \frac{1}{2}(-1 + \eta\cos 2\phi) \\ V_{zz} &= \frac{1}{2}(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi) \\ V_{xy} &= V_{yx} = \frac{1}{2}\eta\cos\theta\sin 2\phi \\ V_{xz} &= V_{zx} = -\frac{1}{2}\sin\theta\cos\theta(3 + \eta\cos 2\phi) \end{aligned} \quad (3)$$

In the previous expressions, θ and ϕ are the polar angles describing the orientation of the EFG tensor with respect to the magnetic field and η is the quadrupolar asymmetry parameter which is defined as $(V_{11} - V_{22})/V_{33}$ and can take values ranging from 0 to 1, where 0 corresponds to an axially symmetric tensor. An alternative parameter is the quadrupolar frequency (ν_Q) which is defined as follows:

$$\nu_Q = \frac{3C_Q\sqrt{1 + \frac{\eta^2}{3}}}{2I(2I-1)} \quad (4)$$

It can be useful to compare ν_Q to ν_0 in order to judge whether a particular spin system should be described in the context of NMR or NQR.

Note that in the Hamiltonian, the secular approximation was used to define the chemical shift interaction; in other words, the antisymmetric parts [27,28] of the chemical shift were ignored. The angular dependence of the chemical shift interaction is

contained in the value of δ_{ZZ} , which is calculated as follows:

$$\delta_{ZZ} = \delta_{11}\sin^2\vartheta\cos^2\varphi + \delta_{22}\sin^2\vartheta\sin^2\varphi + \delta_{33}\cos^2\vartheta, \quad (5)$$

where the polar angles ϑ and φ are used to represent the orientation of the chemical shift (CS) tensor principal axis system with respect to the applied magnetic field and δ_{NN} ($N=1, 2, \text{ or } 3$) are the chemical shift tensor principal components. These tensor components are ordered as $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Note that the polar angles for the CS tensor can be different from those used to orient the EFG tensor although they are tied to one another with the use of Euler angles (see QUEST help file). To define the CS tensor in QUEST, three additional parameters are used: the isotropic chemical shift value (δ_{iso}), the span (Ω), and the skew (κ). These are defined as follows [29]:

$$\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}, \quad (6)$$

$$\Omega \cong \delta_{11} - \delta_{33}, \quad (7)$$

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}. \quad (8)$$

From the quadrupolar Hamiltonian (i.e., the second term in (1)) it can be seen that only its first term commutes with the Zeeman Hamiltonian. All other terms contain the raising and lowering spin operators which have the effect of increasing or decreasing the magnetic quantum number by one unit. This potential problem is more easily understood when we consider the individual elements of the Zeeman-quadrupolar Hamiltonian matrix, which are calculated as follows:

$$\langle m | \hat{H}_{ZQ} | m \rangle = -m \cdot \nu_0(1 + \delta_{ZZ}) + \frac{\sqrt{6}C_Q}{12I(2I-1)}(3m^2 - I(I+1))V_0, \quad (9)$$

$$\langle m \pm 1 | \hat{H}_{ZQ} | m \rangle = \frac{\pm C_Q}{4I(2I-1)}((2m \pm 1)\sqrt{I(I+1) - m(m \pm 1)})V_{\mp 1}, \quad (10)$$

$$\langle m \pm 2 | \hat{H}_{ZQ} | m \rangle = \frac{C_Q}{4I(2I-1)}(\sqrt{I(I+1) - m(m \pm 2)}\sqrt{I(I+1) - m(m \pm 1)})V_{\mp 2}, \quad (11)$$

$$\langle m \pm p | \hat{H}_{ZQ} | m \rangle = 0 \text{ where } p > 2. \quad (12)$$

If the pure Zeeman states were in fact true eigenfunctions of this operator, then all off-diagonal terms would be zero. Although other methods have been proposed [30–38], this problem can also be solved by simply diagonalizing the Hamiltonian matrix. This approach for calculating exactly the eigenvectors of the Hamiltonian for quadrupolar nuclei has found widespread use for the calculation of splittings caused by residual dipolar coupling [39,40]. Rotation of the total spin Hamiltonian matrix is performed in order to re-express it in a frame in which it is diagonal. The true eigenvalues (energy levels) can then be extracted directly and can be used to calculate the resonant transition frequencies. In this new frame, the correct eigenfunctions for the different states have been expanded as a superposition of all Zeeman states [39,40]:

$$|n\rangle = \sum_{m=-I}^I a_{mn}|m\rangle, \quad (13)$$

where a_{mn} is the m th component of the n th eigenvector. These are generated as a result of the diagonalization, and correspond to the columns of the rotation matrix (see QUEST help file).

These eigenfunctions can then be used to calculate all other NMR properties such as dipolar coupling [26]. In QUEST, these are

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