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Shaped pulses in NQR

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Abstract

It is shown here that NQR pulses can be treated in a consistent way leading to expressions based upon SU(2) algebra. The use of various bases (fictitious spin 1/2, spherical tensors) is not necessary. One consequence is that shaped pulses designed for NMR can be used for NQR.

1. Introduction

The calculation of pulses in pure NQR is basically straightforward, but the mathematics become intractable as the spin magnitude increases. To a large extent, this problem has been overcome by the use of computer algebra which permits us to extend the calculations to spins up to $I=7/2$, all within the same approximations. The only approximation that we use is to ignore the non-secular terms in the solution of the time dependence. Having said this, we also note that the choice of basis is important for obtaining the most concise solution. The problem we treat is that of a quadrupole spin with non-zero asymmetry subject to arbitrary rf pulse. The field direction and principal axis frame do not have to coincide, thereby making the results valid for both single crystals and powders. In addition, we allow for arbitrary amplitude and phase modulation. The formulation is developed quite generally, although we allow for a particular amplitude and phase modulation at the end that can lead to either analytical or numerical solutions.

In 1977, Pratt [1] studied the same problem in the interaction representation for a spin 3/2. His method allows for significant simplification in following the spin dynamics but difficulties are encountered in obtaining the complete solution for differential equations which arise in his treatment. From his work it is evident that the response of the quadrupole nuclei is similar to that for a spin 1/2 in NMR. From this seminal work, a variety of other approaches have been presented. One [2] uses a fictitious spin 1/2 bases and another is a spherical tensor approach [3]. These approaches have resulted in lengthy tables of the commutation relationships. Recently Dubey et al. [4] used the set of three operators to describe a spin 3/2 as a linear combination of spin 1/2 operators to study NQR zero time resolution technique interaction representation. The basis he uses is diagonal in the quadrupole Hamiltonian and the commutation relations obtained for the dynamics are relatively simple. Generalization to higher spins, however, does not appear to retain this simplicity.

Our approach is to recognize that the NQR pulses are selective, acting between two pairs of adjacent levels [5]. We too introduce the representation in which the quadrupole Hamiltonian for spin 3/2 is diagonal and for which the total Hamiltonian (including rf Hamiltonian) is block diagonal. Each block is recognized to be a simple SU(2) Hamiltonian well known for the NMR spin 1/2 cases. Hence, the effect

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of the pulse can be treated as a rotation with the only difference with NMR being that the rf amplitude is replaced by the effective rf frequency as the result of the selectivity of the pulse. Our treatment is not restricted to spin 3/2 and can be easily generalized for higher-order half integer spins. We present only the 3/2 case in order to be concise and to illustrate the approach. In fact we have the results for up to $I=7/2$. For higher-order spins, we introduce the representation where the quadrupole Hamiltonian is diagonal. The energy splittings between pairs of degenerate levels of a half integer spin greater than 3/2 are unequal and the rf pulse affects only one transition. If the carrier frequency of an rf pulse is close to the frequency of one of the transitions, then we define a reduced matrix for the quadrupoles and rf Hamiltonians which includes only these pairs of states. Other states are not affected by the pulse. Thus the problem reduces from $(2I+1)\times(2I+1)$ to 4×4 matrix. Thus the total reduced Hamiltonian for any spin can be brought to the block diagonal form and treated as for spin 3/2. In each case a transition reduced by the rf field has a specific effective rf frequency which is a function of the spin quantum numbers I, M, the asymmetry parameter η as well as the orientation of the rf coil. In this regard, NQR is different from NMR, and, in particular, the treatment by Samoson and Lippmaa [6].

As mentioned above we also introduce amplitude and phase modulation to NQR in a consistent and general way. Customarily, NQR spectroscopists use constant envelope pulses. A single short rf pulse does not excite the broad NQR spectra uniformly. A useful excitation profile should be complete, localized and uniform. We found that the well-known hyperbolic secant pulse performs well in the case of a single crystal. In powders, the response to a hyperbolic secant pulse is significantly superior to a single pulse even on resonance. In fact, we find the performance of the hyperbolic secant for powders is superior in profile than any of the composite pulse sequences studied to date [7]. Another advantage of the shaped pulses is that they are relatively short when compared with composite pulses. This is useful since lengthy composite pulse sequences are not desirable in NQR because of the much shorter spin relaxation times T_1 and T_2 than those in the usual NMR situation.

2. Theoretical background

We shall use in this Letter a simple spin 3/2 example to describe the evolution of the quadrupole system under the influence of the shaped pulse. The Hamiltonian in the quadrupole principal axis system (QPAS) is given as

$$H_T = H_Q + H_{rf}\,, \tag{1}$$

where

$$H_Q = \frac{\hbar e^2 qQ}{4I(2I-1)}\,[3I_z^2 - I^2 + \tfrac{1}{2}\eta(I_+^2 + I_-^2)]$$

is the pure quadrupole Hamiltonian and

$$H_{rf} = -2\hbar\omega_1(t)\cos[\omega t - \phi(t)]\,(\cos\phi_L \sin\theta_L\, I_x + \sin\phi_L \sin\theta_L\, I_y + \cos\theta_L\, I_z)$$

is the radiofrequency Hamiltonian. Here e^2qQ is the nuclear quadrupole coupling constant, and the angles θ_L and ϕ_L specify the orientation of the rf field with respect to the QPAS system of the crystal in the powder sample.

The quadrupole Hamiltonian is diagonalized by the unitary transformation S (see Eq. (4) of Ref. [4]). In this new basis $|\psi\rangle = S^t|IM\rangle$, the quadrupole Hamiltonian is

$$H_Q^\psi \propto \tfrac{1}{2}\hbar\omega_Q R \tag{2}$$

where $\omega_Q = \frac{1}{2}e^2qQ(1+\frac{1}{3}\eta^2)^{1/2}$ and the matrix R has diagonal elements of $(1, -1, -1, 1)$. Following Pratt [1], the interaction picture is introduced by the operator Π,

$$\Pi = \exp(-\tfrac{1}{2}\mathrm{i}\omega t R)\,. \tag{3}$$

Transforming H_{rf}^ψ by Π and neglecting high frequency terms results in

$$\tilde{H}_{rf}^\psi = -\tfrac{1}{2}\hbar\omega_1 \left[\begin{pmatrix} 0 & \alpha-\mathrm{i}\beta & \gamma & 0 \\ \alpha+\mathrm{i}\beta & 0 & 0 & -\gamma \\ \gamma & 0 & 0 & \alpha-\mathrm{i}\beta \\ 0 & -\gamma & \alpha+\mathrm{i}\beta & 0 \end{pmatrix}\cos\phi + \begin{pmatrix} 0 & -\mathrm{i}\alpha-\beta & -\mathrm{i}\gamma & 0 \\ \mathrm{i}\alpha-\beta & 0 & 0 & -\mathrm{i}\gamma \\ \mathrm{i}\gamma & 0 & 0 & \mathrm{i}\alpha+\beta \\ 0 & \mathrm{i}\gamma & -\mathrm{i}\alpha+\beta & 0 \end{pmatrix}\sin\phi\right], \tag{4}$$

where

$$\alpha = \frac{3+\eta}{(3+\eta^2)^{1/2}} \sin\theta_L \cos\phi_L ,$$

$$\beta = \frac{3-\eta}{(3+\eta^2)^{1/2}} \sin\theta_L \sin\phi_L ,$$

$$\gamma = -\frac{2\eta}{(3+\eta^2)^{1/2}} \cos\theta_L .$$

The total Hamiltonian $\tilde{H}^{\Psi}_T$ in the interaction picture can be brought to the block-diagonal form by means of the following unitary transformation,

$$|\psi'\rangle = T|\psi\rangle ,$$

$$T = \begin{bmatrix} \frac{\gamma}{\sqrt{(\alpha^2+\beta^2+\gamma^2)}} & 0 & 0 & \frac{\alpha-i\beta}{\sqrt{(\alpha^2+\beta^2+\gamma^2)}} \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -\frac{\alpha+i\beta}{\sqrt{(\alpha^2+\beta^2+\gamma^2)}} & 0 & 0 & \frac{\gamma}{\sqrt{(\alpha^2+\beta^2+\gamma^2)}} \end{bmatrix} , \tag{5}$$

to give $\tilde{H}^{\Psi'}_T = T\tilde{H}^{\Psi}_T T^{\dagger}$ with

$$h_1 = \tfrac{1}{2}\hbar(\omega_Q - \omega)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \tfrac{1}{2}\hbar\omega_{1\mathrm{eff}}\begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix},$$

$$h_2 = -\tfrac{1}{2}\hbar(\omega_Q - \omega)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \tfrac{1}{2}\hbar\omega_{1\mathrm{eff}}\begin{pmatrix} 0 & e^{i\phi} \\ e^{-i\phi} & 0 \end{pmatrix}, \tag{6}$$

and $\omega_{1\mathrm{eff}} = \omega_1(t)\sqrt{(\alpha^2+\beta^2+\gamma^2)}$. The Hamiltonians h_1 and h_2 are SU(2) Hamiltonians for the elementary spin 1/2 problem. The transformation T effectively decomposes the spin 3/2 algebra into the direct product of two SU(2) algebras. The spin density matrix in the $|\psi\rangle$ basis is initially diagonal and

$$\rho(0) \propto R . \tag{7}$$

The transformation T leaves the matrix R unchanged. The evolution of the density matrix $\tilde{\rho}(t)$ in the interaction picture with the pulse on is described by the Liouville equation

$$i\hbar \frac{\partial\tilde{\rho}}{\partial t} = [\tilde{H}^{\Psi'}_T, \tilde{\rho}] \tag{8}$$

or using Eq. (6)

$$i\hbar \frac{\partial\tilde{\rho}_k}{\partial t} = [h_k, \tilde{\rho}_k] , \quad k = 1, 2 , \tag{9}$$

where $\tilde{\rho}(t) = \begin{pmatrix} \tilde{\rho}_1 & 0 \\ 0 & \tilde{\rho}_2 \end{pmatrix}$ with the initial condition given by Eq. (7). The general solution to Eq. (9) is of the form

$$\tilde{\rho}_1(t) \propto \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{12}^* & -\sigma_{11} \end{pmatrix},$$

$$\tilde{\rho}_2(t) \propto \begin{pmatrix} -\sigma_{11} & \sigma_{12}^* \\ \sigma_{12} & \sigma_{11} \end{pmatrix}, \tag{10}$$

with $\sigma_{11}^2 + |\sigma_{12}|^2 = 1$. The only approximation made is the truncation of high frequency terms, the price of which is that corrections of the order of Bloch–Siegert shifts are ignored [8]. The inversion signal is defined as

$$W_1 = \mathrm{tr}[R\tilde{\rho}(t)] \propto \sigma_{11} . \tag{11}$$

Let $f = \sigma_{12}^*/(1+\sigma_{11})$. Eq. (9) with $k=1$ is then transformed into the Bloch–Riccati equation

$$\dot{f} + i\Delta\omega f - \tfrac{1}{2}i\Omega^*(t) f^2 + \tfrac{1}{2}i\Omega(t) = 0 , \tag{12}$$

where $\Omega(t) = \omega_{1\mathrm{eff}} e^{i\phi(t)}$. In general, Eq. (12) is not solvable analytically for arbitrary amplitude and phase modulation expressed in $\omega_1(t)$ and $\phi(t)$. However, it is possible to solve (12) analytically in some special cases such as rectangular, modulated hyperbolic secant and exponentially varying pulses [9].

For a rectangular pulse where the amplitude and the phase are constants, we have

$$\sigma_{11} = \frac{1}{\Omega^2}[\omega_{1\mathrm{eff}}^2 \cos(\Omega t) + \Delta\omega^2] , \tag{13}$$

where $\Omega = \sqrt{\Delta\omega^2 + \omega_{1\mathrm{eff}}^2}$.

Consider next a hyperbolic secant pulse which gives

$$\Omega(t) = \Omega_{0\mathrm{eff}}[\mathrm{sech}\,\beta(t-t_0)]^{1+i\mu} \tag{14}$$

with $\Omega_{0\mathrm{eff}} = \Omega_0\sqrt{(\alpha^2+\beta^2+\gamma^2)}$ where μ is a real constant and Ω_0 is the pulse amplitude. The solution for this pulse shape was found to be [10]

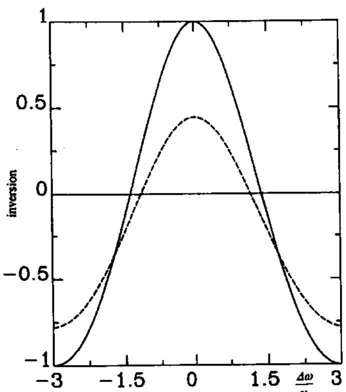

Fig. 1. Single constant amplitude and phase π pulse, $\omega_1 = 50$ kHz. This pulse scales as $\Delta\omega/\omega_1$. To compare with Fig. 2, set $\omega_1 = 50$ kHz.

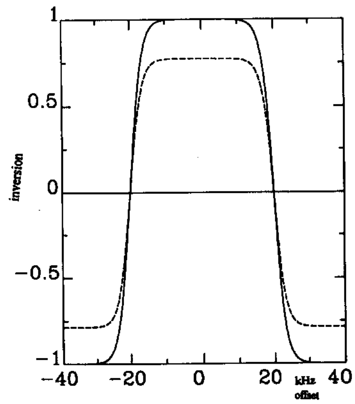

Fig. 2. Hyperbolic secant π pulse with $\mu = 5.0$, $\beta\mu = 25$ kHz, $\Omega_0 = 50$ kHz. This pulse does not scale as $\Delta\omega/\omega_1$.

$$\sigma_{11} = \tanh \pi\left(\frac{\Delta\omega}{2\beta} + \frac{\mu}{2}\right) \tanh \pi\left(\frac{\Delta\omega}{2\beta} - \frac{\mu}{2}\right) + \cos\{\pi[(\Omega_{0\text{eff}}/\beta)^2 - \mu^2]^{1/2}\} \times \operatorname{sech} \pi\left(\frac{\Delta\omega}{2\beta} + \frac{\mu}{2}\right) \operatorname{sech} \pi\left(\frac{\Delta\omega}{2\beta} - \frac{\mu}{2}\right). \quad (15)$$

The significant extention and difference between this work and that of Ref. [10] is the appearance of $\Omega_{0\text{eff}}$ which reflects the orientation of the quadrupole crystal with respect to QPAS. Thus (15) is applicable to powders as well as single crystals. For $\Omega_{0\text{eff}} \geqslant \mu\beta$, $\mu \geqslant 2$ the localized inversion is of width $\Delta\omega = \pm\mu\beta$.

Considering powder samples, if the distribution is assumed to be random then the averaged signal is

$$W \propto \int \sin\theta_L \, \sigma_{11} \frac{\sin\theta_L \, d\theta_L \, d\phi_L}{4\pi}. \quad (16)$$

Figs. 1 and 2 show the inversion profiles for rectangular and hyperbolic secant pulses. The dashed lines indicate the responses of powders. The remarkable insensitivity of the hyperbolic secant pulse to the amplitude of the rf field makes it superior to rectangular pulses even when the pulse is on-resonance for powders. In fact, we conclude that the hyperbolic secant pulse works better for powders than any composite pulse sequence known to date [7].

3. Conclusions

Our treatment here is not restricted to spin 3/2. The pulse in NQR is selective being between two pairs of levels for half integer spins. For higher-order half integer spins, the reduced matrices for the quadrupole and rf Hamiltonians for each transition have the same form as in e.g. (2) and (4) with appropriate α, β, γ and ω_Q. The effect of the pulse can be treated as a pure rotation with appropriate effective frequency.

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