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Theory of pulses in nuclear quadrupole resonance spectroscopy

I. Physical picture

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The effect of radiofrequency pulses in nuclear quadrupole resonance (NQR) spectroscopy is examined. The description is different from that needed in nuclear magnetic resonance (NMR) spectroscopy. In particular, both rotating and counter-rotating radiofrequency field components are retained. Pulses in NQR spectroscopy are selective and cause transitions between two pairs of levels $(\pm M) \rightarrow \pm(M+1)$, other transitions are not normally excited. The formulation of pulses is then described for any spin I by two 2×2 rotation matrices, one causing an $M \rightarrow M+1$ transition and the other causing a $-(M+1) \rightarrow -M$ transition. Calculations on resonance for spins with an axially symmetric nuclear quadrupole for up to three pulses are presented for spins $I = 1$ and $I = 3/2$. The results agree with the work of Reddy, R. and Narasimhan, P. T., 1991, *Molec. Phys.*, **72**, 491, in the appropriate limits.

1. Introduction

Nuclear quadrupole resonance (NQR) is the transient and echo response arising from pulsing nuclear spins in zero or small magnetic fields [1]. These pulses are bursts of radiofrequency (RF) energy at, or close to, certain nuclear resonances, and cause transitions between levels which have predominantly zero-field splittings. The strongest of such interactions for spins with magnitude $I > 1/2$ is usually the nuclear electric quadrupole interaction, although many interactions are possible [2, 3]. From NQR studies, information about the local electric field gradients and nuclear motions can be obtained.

Since the pioneering work of Bloom *et al.* [4, 5], various formulations of NQR have emerged [5–7]. It is well established that a spin density matrix formalism is convenient for describing the time development of spins in NQR spectroscopy, for the same reason that it is used in NMR, namely, to describe coherences properly [8]. As for any quantum mechanical problem, a judicious choice of basis operators, which span the operator space, can lead to both greater physical insight and simpler mathematics than a poorly chosen operator basis set. Different bases have advantages for different physical situations involving nuclear spin. The fictitious spin-1/2 formalism has been used extensively in NMR to describe multiple quantum processes [9–13]. For selective excitation, Cartesian single transition operators have been particularly useful [14]. Various product operator bases are used in both NMR and NQR, particularly when dipole–dipole interactions are important [15–17]. Spherical tensor operators are convenient in the case of NMR, because of a large static Zeeman field which gives a dominant direction [18–24]. Pulses are physically and mathematically described as rotations in this basis. Spherical tensor operators are *not* particularly convenient for describing evolution under a quadrupole interaction although, for a small axially symmetric quadrupole with a dominant Zeeman term, this disadvantage is outweighed by the facility of treating pulses as rotations in a spherical basis [19, 23]. Another advantage of spherical tensor operators is the associated well-known Clebsch–Gordan algebra [25, 26]. This allows concise and general commutation relations to be generated for all spin magnitudes, thereby avoiding long tables of relations. Such tables are, nevertheless, found in the treatment of Bowden *et al.* [27, 28], who use a pseudospherical tensor basis. That is, they use symmetric $(T^{kq} + T^{k-q})$ and antisymmetric $(T^{kq} - T^{k-q})$ combinations of spherical components of irreducible tensor operators. Bowden *et al.*'s work has been used by Reddy and Narasimhan to study pulses in NQR [29].

This paper also describes pulses in NQR. For this case, in contrast to reference [29], we find a spherical tensor operator basis to be inconvenient. The main reasons are that spherical tensors hide the physical visualization of NQR pulses. In addition, the mathematics is quite straightforward, with all single quantum excitation pulses being describable by a simple 2×2 rotation matrix. That is, this formalism projects out two pairs of energy levels, each of which is described by SU(2) algebra (Pauli spin matrices). As such, this method is closely related to that of single transition operators [14] and fictitious spin-1/2 operators [10]. There is no large z magnetization in NQR experiments, and the quadrupole interaction dominates. Hence, the best basis is that which is diagonal in the quadrupole interaction H_Q. This is the $|IM\rangle\langle IM'|$ basis for axially symmetric quadrupole interaction. For non-axially symmetric interaction and in the presence of magnetic fields, the corresponding basis functions are linear combinations of the basis elements $|IM\rangle\langle IM'|$. The basis $|IM\rangle\langle IM'|$ is also convenient for describing NQR pulses, which are different in a number of ways from those in NMR. The major difference is that a pulse causes only a single quantum *selective* excitation in NQR [13, 30]. In this case, the basis $|IM\rangle\langle IM'|$ enables us to describe a pulse by a Wigner rotation matrix $D^{(1/2)}$ among two levels.

By using this approach, a simple picture emerges which is summarized in section 2. This is followed in section 3 with a detailed description of a Zeeman-like Hamiltonian needed for NQR pulses. Both integral and half-integral spins are treated simultaneously in section 4 while section 5 contains results for two and three pulses.

Not treated here are non-axially symmetric quadrupole interactions, which will be considered in the future. Although it is recognized that $\eta \neq 0$ is an important case in NQR (where η is the asymmetry parameter [3]), this case is not treated here in the interest of clarity. Including $\eta \neq 0$ is straightforward for those cases for which the eigenvalues and eigenfunctions for the nuclear quadrupole Hamiltonian are known. Therefore, in this paper, the nuclear quadrupole for

$\eta = 0$ is taken as

$$H_Q = -\frac{\hbar e^2 Qq}{4I(2I-1)}[I^2 - 3I_z^2] \tag{1}$$

which is diagonal in the $|IM\rangle\langle IM'|$ basis. The quantity e^2Qq is the quadrupole coupling constant [3].

2. Description of pulses in NQR

NQR experiments now rely on pulsed techniques. A sample is placed in a coil, thereby defining a laboratory axis, say the $\hat{x}$ axis, and bursts of RF field along this axis, perpendicular to the $\hat{z}$ direction, cause transitions between nuclear levels when the carrier frequency is close to that of the nuclear splittings. Free induction decays (FIDs) and, for multiple pulses, echoes can be detected.

In the NMR case, a resonant pulse of certain duration can produce a rotation of the magnetization vector, initially aligned along the direction of the large static field ($\hat{z}$ axis), through any desired angle. A 90° resonant pulse puts the magnetization in the xy plane and the phase ϕ of the pulse determines where in the xy plane the magnetization vector points.

In NQR, no such magnetization vector exists. Rather, the nuclear quadrupoles are aligned along a principal axis and described, not by a vector, but by an average over a second rank tensor. In the axially symmetric case, the laboratory $\hat{z}$ axis and the principal axis can coincide. A "90°" pulse in NQR is usually described as a pulse of duration such that the resulting FID is maximized.

A pulse along the x axis in NMR causes a coherent oscillation between Zeeman levels causing all the spin vectors to precess in the zy plane. Interrupting the pulse, after an appropriate time, leaves the spins coherently aligned along the y axis: this is a 90° pulse. Figure 1(a) shows a linear Zeeman splitting, and the transitions responsible for a nonselective NMR pulse. Note that all transitions are single quantum; from one M level up to the next. All splittings are approximately equal and have associated with them a Larmor frequency ω_0. Figure 1(a) therefore represents a resonant nonselective NMR pulse.

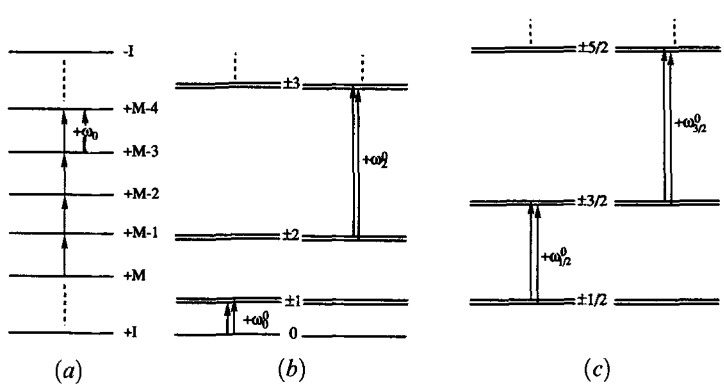

Figure 1. (a) NMR pulse showing single quantum transitions. (b) NQR pulses in integer spins: transitions $0 \rightarrow 1$, $0 \rightarrow -1$, $2 \rightarrow 3$ and $-2 \rightarrow -3$. (c) Two examples of NQR pulses in half-integer spins: transitions $1/2 \rightarrow 3/2$, $-1/2 \rightarrow -3/2$ and $3/2 \rightarrow 5/2$, $-3/2 \rightarrow -5/2$.

Figure 1(b, c) shows the zero-field NQR case. The energy level splittings are unequal and transitions occur selectively. These figures show integer and half-integer spin cases. In contrast to the NMR case, the RF field causes two single quantum transitions. One is $M \rightarrow M+1$, with frequency, say, ω_M^0, while the other is $-(M+1) \rightarrow -M$ with frequency $-\omega_M^0$. NQR pulses are, therefore, selective and require two transitions of equal frequency magnitude, but relatively of opposite sign.

Applied in the NQR case on spins initially at equilibrium, a pulse partially destroys the quadrupole alignment, thereby producing polarizations of different tensor rank. Among these is a nuclear vector component which is detected as a FID. The magnitude of the FID depends on the characteristics of the pulse and the spin system.

The difference between the NMR and the NQR cases can be understood in terms of the RF magnetic field. A coil orientated along the x axis produces an RF field $\boldsymbol{H}(t)$ with a carrier frequency ω, amplitude H_1 and phase ϕ given by

$$\boldsymbol{H}(t) = 2\hat{x}H_1 \cos(\omega t - \phi). \tag{2}$$

This can be decomposed into two components rotating in the opposite senses as

$$\begin{aligned} \boldsymbol{H}(t) &= \underbrace{H_1[\hat{x}\cos(\omega t - \phi) - \hat{y}\sin(\omega t - \phi)]}_{\text{Rotating}} + \underbrace{H_1[\hat{x}\cos(\omega t - \phi) + \hat{y}\sin(\omega t - \phi)]}_{\text{Counter-rotating}} \\ &\equiv \boldsymbol{H}^+(t) + \boldsymbol{H}^-(t). \end{aligned} \tag{3}$$

Note that resonance is defined here as $\omega = \omega_0$, in contrast to Slichter [8], who defines resonance for $\omega = -\omega_0$. The part "rotating" in equation (3) describes the component that causes a transition between levels of frequency ω, in a clockwise sense. The part "counter-rotating" in equation (3) describes the component that causes transitions between levels of frequency $-\omega$, in the anticlockwise sense.

In NMR, only the rotating component need be retained (if $\omega_0 = \gamma H_0$). This term is constant in a frame of reference rotating with the Larmor frequency ω_0, i.e., $\omega = \omega_0$. In contrast, the counter-rotating component is then off-resonant by $2\omega_0$ and is usually dropped in treatments of NMR. Hence, from figure 1(a), all the transitions from $M+1 \rightarrow M$ are caused by the component rotating in phase with the natural Larmor frequency. The counter-rotating component, if retained, leads to Bloch–Siegert shifts [31, 32].

In NQR, both rotating and counter-rotating components must be retained for both integer and half-integer spins. The rotating component in equation (3) causes transitions from $M \rightarrow (M+1)$ with frequency ω_M^0. The other component, rotating in the opposite sense, is again off-resonant by $2\omega_M^0$ for this transition. The counter-rotating component, however, does cause the transition from $-M \rightarrow -(M+1)$ with frequency ω_M^0.

A pulse in NQR may thus be visualized as causing transitions between two degenerate (or nearly degenerate, when there are small magnetic fields, axially asymmetric quadrupolar effects) pairs of levels. One is 'up' ($\Delta M = 1$) with positive frequency and the other is 'down' ($\Delta M = -1$) also with positive frequency. Ignoring small effects of the order of Bloch–Siegert shifts means that the two transitions are uncoupled and independent. An NQR pulse can, therefore, be thought of as causing two 2×2 submatrices of the $(2I+1) \times (2I+1)$ dimensional spin density matrix to evolve without affecting the other states. This idea is visualized in figure 2 and shows how double resonance in NQR can be viewed.

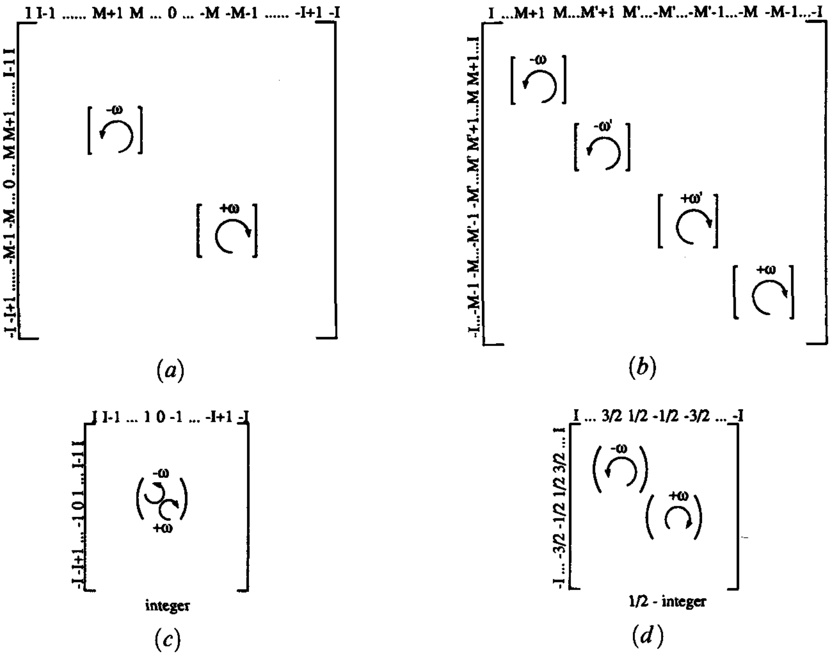

Figure 2. (*a*) Visualization of rotating and counter-rotating components for transitions $-M \rightarrow -(M+1)$ and $M \rightarrow M+1$. (*b*) Examples of double resonance-type experiments. (*c*) Rotating and counter-rotating components for transitions $0 \rightarrow 1$ and $0 \rightarrow -1$. (*d*) Rotating and counter-rotating components for transitions $-1/2 \rightarrow -3/2$ and $1/2 \rightarrow 3/2$.

In addition, as seen from figure 1(*b, c*), these pulses are selective, and single quantum. As such, these pulses can be viewed as acting on a fictitious spin-1/2 or a pair of levels. As is well-known [9, 20], selective pulses have the RF amplitude ω_1 replaced by an effective RF amplitude $\omega_{1,\text{eff}}$ given by

$$\omega_{1,\text{eff}} = \sqrt{[(I+M)(I-M+1)]}\omega_1 \qquad (4)$$

for transition $M \rightarrow (M-1)$. A similar effect is found for other interactions [20]. For example, for the quadrupole interaction, the quadrupole coupling constant ω_Q (see eqn. (5)) in (1) must be replaced by an effective coupling constant $\omega_{Q,\text{eff}}$ for selective excitation. As shown in [20] and verified experimentally [33], single quantum selective excitation involving spin systems of magnitude I has a zero quadrupole interaction. This result is in conformity with the neglect of nonsecular terms in the spin dynamics while the pulse is on. The consequence of this is that no matter what the magnitude of the quadrupole, and no matter if it is axially symmetric or not, evolution under the quadrupole for the pair of levels involved in the transition is *not* significant *while* the pulse acts selectively. Hence, all single quantum NQR pulses are, to a good approximation, "pure" or "hard".

These ideas are formulated more mathematically in the next section.

3. Density matrix of spins for NQR pulses

The energy levels of a nuclear spin of magnitude I with an axially symmetric quadrupole interaction are given by the eigenvalues of equation (1). The frequency

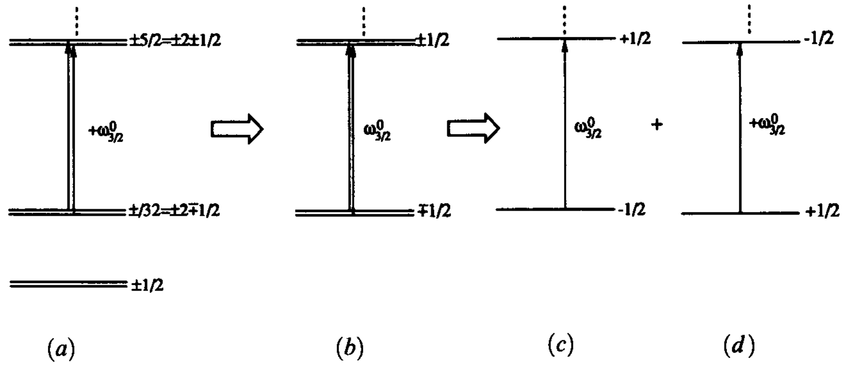

Figure 3. Examples of selective excitation in NQR pulses for half-integer spins. (*a*) Transitions $\pm 3/2 \rightarrow \pm 5/2$. (*b*) Extraction of the two relevant levels. (*c*) Transition from $-1/2 \rightarrow +1/2$ caused by rotating component. (*d*) Transition from $1/2 \rightarrow -1/2$ caused by the counter-rotating component.

between two adjacent levels $\pm M \rightarrow \pm(M+1)$ is

$$\omega_M^0 = \frac{3\omega_Q}{2I(2I-1)}(2M+1), \tag{5}$$

where

$$\omega_Q = \frac{e^2Qq}{2}.$$

In this section, since selective pulses are discussed, only two pairs of levels are treated; these are extracted from the $(2I+1)$ spin manifold shown schematically in figures 3 and 4. Any adjacent degenerate pairs of levels can be written as $\pm M = \pm C \mp 1/2$ and $\pm(M+1) = \pm C \pm 1/2$ for some constant C. In figure 3(*b*), C is equal to 2. These pairs can then be treated as two separate pairs of spin 1/2 having fictitious "gyromagnetic ratios", of opposite magnitude although, in fact, the splitting is due entirely to a quadrupole interaction.

The Hamiltonian for selective excitation can be written, using equation (3), as a sum of two terms, namely

$$\boldsymbol{H}_M(t) = -\gamma\hbar \boldsymbol{I}\cdot[\boldsymbol{H}^+(t) + \boldsymbol{H}^-(t)] = \boldsymbol{H}_M^+(t) + \boldsymbol{H}_M^-(t), \tag{6}$$

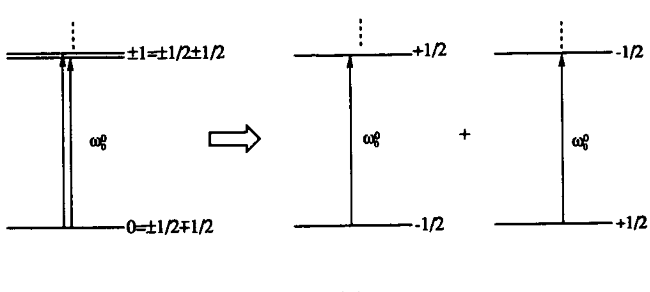

Figure 4. Examples of selective excitation in NQR pulses for integer spins. (*a*) Transitions $0 \rightarrow \pm 1$. (*b*) Transition from $-1/2 \rightarrow +1/2$ caused by rotating component. (*c*) Transition from $1/2 \rightarrow -1/2$ caused by the counter-rotating component.

where the Hamiltonians $H_M^{\pm}(t)$ have the same form as that due to a sum of Zeeman and RF field terms,

$$H_M^{\pm}(t) = \mp\hbar\omega_M^0 I_z - \hbar\omega_{1,\mathrm{eff}}[I_x \cos(\omega t - \phi) \mp I_y \sin(\omega t - \phi)]. \tag{7}$$

In equation (7), the quantities I_x, I_y and I_z are the spin components of a fictitious spin 1/2 associated with levels $\pm M$ and $\pm(M+1)$. They can be represented by 2×2 matrices proportional to the Pauli spin matrices. Although the distinction is not made explicitly in equation (7), the spin components for $H_M^+(t)$ and $H_M^-(t)$ refer to different fictitious spins 1/2.

From equation (7), it can be seen that the transitions induced by one component of the field can be obtained from the other as follows,

$$H_M^+(t) \to H_M^-(t) \qquad \text{as } \omega_M^0 \to -\omega_M^0, \omega \to -\omega \text{ and } \phi \to -\phi.$$

Hence, it is only necessary to solve for one RF component and then transform the result using the above to obtain the second solution. In fact, the NMR case can be used, which from figure 1(a), uses the Hamiltonian $H_M^+(t)$. It is particularly simple, since the solution is needed only for a spin-1/2 case. The results are summarized below.

The density operator for any particular time t, $\sigma_{1/2}(t)$, for a spin 1/2 may be written in the basis of spherical components of irreducible tensor operators $\mathscr{Y}^{(k)q}(I)$ as

$$\sigma_{1/2}(t) = \tfrac{1}{2}\left[E_{1/2} + \sum_{q=-1}^{1} \mathscr{Y}^{(1)q}(1/2)\phi_q^1(t)\right], \tag{8}$$

where $\phi_q^1(t)$ is the expectation value of $\mathscr{Y}^{(1)q}(1/2)$ [18]. $E_{1/2}$ is a 2×2 identity matrix. In the $|IM\rangle\langle IM'|$ basis of a spin 1/2, the operators have the following matrix representations,

$$\mathscr{Y}^{(1)0}(1/2) = i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{9}$$

$$\mathscr{Y}^{(1)1}(1/2) = -i\sqrt{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{10}$$

and

$$\mathscr{Y}^{(1)-1}(1/2) = i\sqrt{2}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \tag{11}$$

The time dependence of the polarizations $\phi_q^1(t)$ is obtained by solving the von Neumann equation

$$i\hbar\frac{\partial\sigma_{1/2}(t)}{\partial t} = [H(t), \sigma_{1/2}(t)]. \tag{12}$$

This has been done exactly for the Hamiltonian $H_M^+(t)$ for any spin magnitude (using the corresponding density matrix for a spin I) and for both on- and off-resonance [20, 34]. The solution is given in terms of a Wigner rotation matrix $D^{(1)}(\alpha\beta\gamma)$. We shall denote the density matrices which evolve under the Hamiltonians $H_M^{\pm}(t)$ by $\sigma^{\pm}(t)$ here and the respective polarizations $\phi_q^{(1)}(t)$ by $\phi_q^{\pm}(t)$. First, we denote a rotating (counter-rotating) frame by

$$\hat{\phi}_q^{\pm}(t) = \exp(\mp i\omega q t)\phi_q^{\pm}(t). \tag{13}$$

Note the difference between two components rotating with opposite senses. The time dependence of $\hat{\phi}_q^+(t)$, for example, is given explicitly by

$$\hat{\phi}_q^+(t) = \sum_{q'=-1}^{1} \boldsymbol{D}_{qq'}^{(1)}(\alpha^+ + \phi, \beta, \alpha^+ - \phi + \pi)\hat{\phi}_{q'}^+(0) \tag{14}$$

where the angles α^+, β and resonance offset $\Delta\omega$ are

$$\alpha^+ = -\tan^{-1}\left[\frac{\Delta\omega}{\Omega}\tan\left(\frac{\Omega t}{2}\right)\right] - \frac{\pi}{2}$$

$$\cos\beta = \frac{1}{\Omega^2}\left[\omega_{1,\text{eff}}^2 \cos\Omega t + \Delta\omega^2\right]$$

$$\Omega = \surd(\Delta\omega^2 + \omega_{1,\text{eff}}^2)$$

and

$$\Delta\omega = \omega - \omega_M^0.$$

The time dependence of the polarization $\hat{\phi}_q^-(t)$ associated with $\boldsymbol{H}_M^-(t)$ can be obtained from that of $\hat{\phi}_q^+(t)$ by using the conditions immediately following equation (7). Explicitly, one obtains,

$$\hat{\phi}_q^-(t) = \sum_{q'=-1}^{1} \boldsymbol{D}_{qq'}^{(1)}(\alpha^- - \phi, \beta, \alpha^- + \phi + \pi)\hat{\phi}_{q'}^-(0), \tag{15}$$

where

$$\alpha^- = \tan^{-1}\left[\frac{\Delta\omega}{\Omega}\tan\left(\frac{\Omega t}{2}\right)\right] - \frac{\pi}{2},$$

is obtained from α^+ by changing the sign of $\Delta\omega$. The angle β is unaltered in the above. When the carrier frequency ω is set equal to ω_M^0, $\Delta\omega = 0$ and this condition is called resonance in the NQR context. It is relevant to point out here that this is different from that of Reddy and Narasimhan (who use the definition $\Delta\omega = \omega_1$) and with whose results we shall compare. On resonance, the angles $\alpha^\pm$ and β become,

$$\alpha^\pm = -\frac{\pi}{2} \text{ and } \beta = \omega_{1,\text{eff}}t.$$

The only differences, therefore, between the two components on resonance are the phase shift ϕ of the RF field, which changes sign, and the frequency $\omega = \omega_M^0$ of the rotating frame, which also changes sign. The solutions given by equations (14) and (15) can be put back into equation (8) and a matrix representation for $\sigma^\pm(t)$ obtained with the use of equation (13) and the 3×3 matrix representation of the Wigner rotation operator $\boldsymbol{D}^{(1)}(\alpha\beta\gamma)$. The final results are given below,

$$\sigma^\pm(t) = \tfrac{1}{2}\left[E_{1/2} + \sum_{q,q'=-1}^{1} \exp(\pm i\omega_M^0 qt)\, \mathscr{Y}^{(1)q}(1/2) \right.$$
$$\left. \times \{\boldsymbol{D}_{qq'}^{(1)}(\alpha^\pm \pm \phi, \beta, \alpha^\pm \mp \phi + \pi)\phi_{q'}^\pm(0)\}\right]. \tag{16}$$

For later use, not just for the cases treated in this paper, but for any treatment of pulsed NQR, explicit matrix representations in the $|IM\rangle\langle IM'|$ basis are needed. For $\sigma^\pm(t)$, there are three terms each, corresponding to the sum over q in the above equation. There are a total of 6 matrices corresponding to the initial conditions $\phi_1^\pm(0)$, $\phi_0^\pm(0)$ and $\phi_{-1}^\pm(0)$. These matrices are obtained from equation (15) by substitution of the Wigner rotation matrix $\boldsymbol{D}^{(1)}(\alpha\beta\gamma)$ [26]

$$\boldsymbol{D}^{(1)}(\alpha\beta\gamma) = \begin{pmatrix} \frac{1}{2}(1+\cos\beta)\exp(i(\alpha+\gamma)) & \frac{1}{\sqrt{2}}\sin\beta\exp(i\gamma) & \frac{1}{2}(1-\cos\beta)\exp(i(\gamma-\alpha)) \\ -\frac{1}{\sqrt{2}}\sin\beta\exp(i\alpha) & \cos\beta & \frac{1}{\sqrt{2}}\sin\beta\exp(-i\alpha) \\ \frac{1}{2}(1-\cos\beta)\exp(i(\alpha-\gamma)) & -\frac{1}{\sqrt{2}}\sin\beta\exp(-i\gamma) & \frac{1}{2}(1+\cos\beta)\exp(-i(\alpha+\gamma)) \end{pmatrix} \tag{17}$$

and the operators in equations (9–11) in the $|IM\rangle\langle IM'|$ basis. They are denoted by $M_q^{\pm}(q=1,0,-1)$ and given by the expressions

$$M_0^{\pm}(\alpha^{\pm},\beta,\phi,\omega t) = \begin{pmatrix} i\cos\beta & i\sin\beta\exp(i(\alpha^{\pm}\mp\phi\pm\omega t)) \\ i\sin\beta\exp(-i(\alpha^{\pm}\mp\phi\pm\omega t)) & -i\cos\beta \end{pmatrix}, \tag{18}$$

$$M_1^{\pm}(\alpha^{\pm},\beta,\phi,\omega t) = \begin{pmatrix} -\frac{i}{\sqrt{2}}\sin\beta\exp(i(\alpha^{\pm}\pm\phi)) & \frac{i}{\sqrt{2}}(1+\cos\beta)\exp(i(2\alpha^{\pm}\pm\omega t)) \\ -\frac{i}{\sqrt{2}}(1-\cos\beta)\exp(\pm i(2\phi-\omega t)) & \frac{i}{\sqrt{2}}\sin\beta\exp(i(\alpha^{\pm}\pm\phi)) \end{pmatrix} \tag{19}$$

and

$$M_{-1}^{\pm}(\alpha^{\pm},\beta,\phi,\omega t) = \begin{pmatrix} \frac{i}{\sqrt{2}}\sin\beta\exp(-i(\alpha^{\pm}\pm\phi)) & \frac{i}{\sqrt{2}}(1-\cos\beta)\exp(\mp i(2\phi-\omega t)) \\ -\frac{i}{\sqrt{2}}(1+\cos\beta)\exp(-i(2\alpha^{\pm}\pm\omega t)) & -\frac{i}{\sqrt{2}}\sin\beta\exp(-i(\alpha^{\pm}\pm\phi)) \end{pmatrix}. \tag{20}$$

The resonance case replaces ω by ω_M^0, and $\alpha^{\pm}$ by $-\pi/2$. In terms of $M_q^{\pm}$, the density operator of the fictitious spin 1/2 is expressed as

$$\sigma^{\pm}(t) = \tfrac{1}{2}[E_{1/2} + \phi_0^{\pm}(0)M_0^{\pm}(\alpha^{\pm},\beta,\phi,\omega t) + \phi_1^{\pm}(0)M_1^{\pm}(\alpha^{\pm},\beta,\phi,\omega t) + \phi_{-1}^{\pm}(0)M_{-1}^{\pm}(\alpha^{\pm},\beta,\phi,\omega t)]. \tag{21}$$

The matrices $M_0^{\pm}$, $M_1^{\pm}$ and $M_{-1}^{\pm}$ are simply the 2×2 rotation matrices in the 2-dimensional spin space of the fictitious spins of $I=1/2$ extracted from the $(2I+1)$ manifold. They can also be derived using single transition operators [14] which differ from equations (9–11) by a unitary transformation. To describe the effect of pulses at or slightly off-resonance, on *any* spin I, these six matrices are all that is needed.

4. A single NQR pulse in spin-1 and spin-3/2 systems

In this section, the effect of a single pulse is calculated for spin-1 and spin-3/2 systems to illustrate the method described in the previous section. Following this, some comments are made about the general spin I case. As seen from equation (21) any initial condition can be chosen. The first pulse, however, is usually applied to the equilibrium spin system. In the absence of any magnetic fields, but in the presence of an axially symmetric quadrupole, the equilibrium density operator is given by

$$\sigma_I(0) = \frac{1}{2I+1}[E_I + \mathscr{Y}^{(2)0}(I)\phi_0^{(2)}(0)], \tag{22}$$

where $\mathscr{Y}^{(2)0}(I)$ is the zeroth spherical component of second rank tensor in I, describing the quadrupole alignment

$$\mathscr{Y}^{(2)0}(I) = \sqrt{\left\{\frac{5}{I(I+1)(2I+3)(2I-1)}\right\}}\{I^2 - 3I_z^2\}. \tag{23}$$

The equilibrium value of the alignment $\phi_0^{(2)}(0)$ in equation (22) is left unspecified for now, but evaluated in special cases later when comparisons with other results are made.

Consider first a spin-1 density operator. From the matrix representation of equations (22) and (23) in the $|IM\rangle$ basis, one obtains,

$$\sigma_1(0) = \frac{1}{3}\left[E_1 + \frac{\phi_0^{(2)}(0)}{\sqrt{2}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right] \tag{24}$$

which can be written as

$$\sigma_1(0) = \frac{1}{3}\left[E_1 + \frac{i\phi_0^{(2)}(0)}{\sqrt{2}}\left\{\begin{pmatrix} i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \begin{matrix} 0 & 0 \end{matrix} \\ \begin{matrix} 0 \\ 0 \end{matrix} & i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{pmatrix}\right\}\right]. \tag{25}$$

The 2×2 submatrices are the same as equation (9). In equation (25) the first matrix describes the transition $0 \longrightarrow 1$ which, assuming the ± 1 levels lie above the 0 level, can be seen as the part σ^+ of equation (21) while the second matrix describes the transition $-1 \longrightarrow 0$ and is the part σ^- of equation (21). The 2×2 sub-blocks of equation (21) thus correspond to the operator $\mathscr{Y}^{(1)0}(1/2)$. The quantity $\phi_0^{\pm}(0)$ in equation (21) is now proportional to $\phi_0^2(0)/\sqrt{2}$ and is the only nonzero term that we need. Thus, a pulse of duration t_1^p leads to the following density matrix for spin-1 after time t_1^p if the initial density matrix (i.e., before pulse) corresponds to equation (24),

$$\sigma_1(t_1^p) = \frac{1}{3}\left[E_1 + \frac{i\phi_0^{(2)}(0)}{\sqrt{2}}\left\{\begin{pmatrix} [M_0^+] & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \begin{matrix} 0 & 0 \end{matrix} \\ \begin{matrix} 0 \\ 0 \end{matrix} & [M_0^-] \end{pmatrix}\right\}\right], \tag{26}$$

where

$$M_0^{\pm} \equiv M_0^{\pm}(\alpha^{\pm}, \beta_1, \phi_1, \omega t_1^p)$$
$$\beta_1 = \omega_{1,\mathrm{eff}} t_1^p = \sqrt{2}\omega_1 t_1^p.$$

For the resonance case in which $\omega = \omega_M^0$ and $\alpha^{\pm} = -\pi/2$, $\sigma_1(t_1^p)$ reduces to

$$\sigma_1(t_1^p) = \frac{1}{3}\left[E_1 + \frac{i\phi_0^{(2)}(0)}{\sqrt{2}}\begin{pmatrix} i\cos\beta_1 & \sin\beta_1 \exp(i(\omega_M^0 t_1^p - \phi_1)) & 0 \\ -\sin\beta_1 \exp(-i(\omega_M^0 t_1^p - \phi_1)) & -2i\cos\beta_1 & -\sin\beta_1 \exp(-i(\omega_M^0 t_1^p - \phi_1)) \\ 0 & \sin\beta_1 \exp(i(\omega_M^0 t_1^p - \phi_1)) & i\cos\beta_1 \end{pmatrix}\right]. \tag{27}$$

The evolution of $\sigma_1(t_1^p)$ for the duration t_1 after the pulse under the influence of the quadrupole can be incorporated easily into the above. In this paper, the evolution between pulses is approximated by an axially symmetric quadrupole to illustrate, in a simple manner, the technique of computing the signal after one, two or three pulses. In the $|IM\rangle\langle IM'|$ basis, the components of the density matrix are eigenfunctions of the axially symmetric quadrupolar Hamiltonian and evolve as

$$|IM\rangle\langle IM'|(t) = \exp\left\{\frac{-3i\omega_Q t(M^2 - M'^2)}{2I(2I-1)}\right\}|IM\rangle\langle IM'|(0) \tag{28}$$

which for spin 1 gives $\omega_M^0 = -3\omega_Q/2$. A non-axially symmetric quadrupolar Hamiltonian in the presence of a small magnetic field will be considered in the future. A general method for describing the evolution due to a Hamiltonian which is not diagonal in the $|IM\rangle\langle IM'|$ basis will also be considered in the future.

Using the approximation of an axially symmetric quadrupole, the density operator after an evolution for the time duration t_1 can be written as (see equation (27))

$$\sigma_1(t_1^p + t_1) = \frac{1}{3}\left[E_1 + \frac{i\phi_0^{(2)}(0)}{\sqrt{2}}\begin{pmatrix} i\cos\beta_1 & \sin\beta_1 \exp(i\omega_M^0(t_1^p + t_1) - i\phi_1) & 0 \\ -\sin\beta_1 \exp(-i\omega_M^0(t_1^p + t_1) + i\phi_1) & -2i\cos\beta_1 & -\sin\beta_1 \exp(-i\omega_M^0(t_1^p + t_1) + i\phi_1) \\ 0 & \sin\beta_1 \exp(i\omega_M^0(t_1^p + t_1) - i\phi_1) & i\cos\beta_1 \end{pmatrix}\right]. \tag{29}$$

Either this can be used as the initial condition for subsequent pulses, or the FID can be calculated at this stage. The magnetization is proportional to $\langle I_x\rangle$ or $\langle I_y\rangle$. Hence one needs only take the trace of equation (29) with $\mathscr{Y}^{(1)1}(1)$,

$$\phi^{(1)1}(1)(t_1^p + t_1) = \mathrm{Tr}\,[\sigma_1(t_1^p + t_1)\mathscr{Y}^{(1)1}(1)]. \tag{30}$$

For spin 1

$$\mathscr{Y}^{(1)1}(1) = -\frac{i\sqrt{3}}{2}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \tag{31}$$

giving

$$\phi^{(1)1}(t_1^p + t_1) = -\frac{i\phi_0^{(2)}(0)}{\sqrt{6}}\sin\{\omega_{1,\mathrm{eff}}t_1^p\}\sin\left[\frac{3\omega_Q}{2}(t_1^p + t_1) + \phi_1\right] \tag{32}$$

as the FID for one NQR pulse.

For spin 3/2, the procedure is similar to the spin-1 case. The resonance frequency is $\omega_M^0 = -\omega_Q$ and the equilibrium spin density operator is

$$\sigma_{3/2} = \tfrac{1}{4}[E_{3/2} + \phi_0^{(2)}(0)\mathscr{Y}^{(2)0}(3/2)]$$

$$= \frac{1}{4}\left[E_{3/2} + \phi_0^{(2)}(0)\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}\right]$$

$$= \frac{1}{4}\left[E_{3/2} + i\phi_0^{(2)}(0)\left\{\begin{pmatrix} i\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} & \begin{matrix}0 & 0\\ 0 & 0\end{matrix}\\ \begin{matrix}0 & 0\\ 0 & 0\end{matrix} & \begin{matrix}0 & 0\\ 0 & 0\end{matrix}\end{pmatrix} - \begin{pmatrix} \begin{matrix}0 & 0\\ 0 & 0\end{matrix} & \begin{matrix}0 & 0\\ 0 & 0\end{matrix}\\ \begin{matrix}0 & 0\\ 0 & 0\end{matrix} & i\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\end{pmatrix}\right\}\right]. \tag{33}$$

As in the case of spin 1, the two fictitious spin-1/2, 2 × 2 matrices are rotated by the pulse. Following the pulse, the off-diagonal matrices evolve freely for the duration t_1 giving the following expression for the spin density operator $\sigma_{3/2}(t_1^p + t_1)$ as

$$\sigma_{3/2}(t_1^p + t_1) = \frac{1}{4}\Bigg[E_{3/2} + i\phi_0^{(2)}(0)$$

$$\times\begin{pmatrix} i\cos\beta_1 & \sin\beta_1\exp(i\omega_M^0(t_1^p+t_1) - i\phi_1) & 0 & 0\\ -\sin\beta_1\exp(-i\omega_M^0(t_1^p+t_1) + i\phi_1) & -i\cos\beta_1 & 0 & 0\\ 0 & 0 & -i\cos\beta_1 & -\sin\beta_1\exp(-i\omega_M^0(t_1^p+t_1)+i\phi_1)\\ 0 & 0 & \sin\beta_1\exp(i\omega_M^0(t_1^p+t_1) - i\phi_1) & i\cos\beta_1 \end{pmatrix}\Bigg] \tag{34}$$

where

$$\beta_1 = \omega_{1,\mathrm{eff}}t_1^p = \sqrt{3}\omega_1 t_1^p.$$

From the form of $\mathcal{Y}^{(1)1}(3/2)$ in the $|IM\rangle\langle IM'|$ basis

$$\mathcal{Y}^{(1)1}(3/2) = -i\sqrt{\frac{6}{5}}\begin{pmatrix} 0 & 1 & 0 & 0\\ 0 & 0 & 2/\sqrt{3} & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{pmatrix}, \tag{35}$$

the FID after a single pulse and a free evolution can be written as

$$\phi^{(1)1}(t_1^p + t_1) = -\frac{i\phi_0^{(2)}(0)}{2}\sqrt{\frac{6}{5}}\sin\{\omega_{1,\mathrm{eff}}t_1^p\}\sin[\omega_Q(t_1^p + t_1) + \phi_1]. \tag{36}$$

This result may be compared with the corresponding expression (28) of Reddy and Narasimhan. From

$$\langle\mathcal{Y}^{(1)1}(3/2)\rangle = \phi_1^{(1)} = -i\sqrt{\frac{2}{5}}[\langle I_x\rangle + i\langle I_y\rangle] \tag{37}$$

and using equation (36) we obtain, for the FID,

$$\langle I_x\rangle = \frac{\sqrt{3}}{2}\phi_0^{(2)}(0)\sin\{\sqrt{3}\omega_1 t_1^p\}\sin[\omega_Q(t_1^p + t_1) + \phi_1] \tag{38}$$

and $\langle I_y \rangle = 0$. Upon substituting

$$\phi_0^{(2)}(0) = \frac{\omega_Q}{4kT}, \qquad t_1^\rho + t_1 \approx t_1 = \tau, \qquad \omega_Q = \Delta\omega,$$

$$\sqrt{3}\omega_1 t_1^\rho = \xi \text{ and } \phi_1 = 90^\circ$$

the expression (28) of [29*a*] is recovered.

The above two examples illustrate our method for any spin I. In general, the equilibrium density matrix for an arbitrary spin I is

$$\sigma_I = \frac{1}{2I+1}[E_I + \phi_0^{(2)}(0)\mathcal{Y}^{(2)0}(I)] \tag{39}$$

where the diagonal matrix $\mathcal{Y}^{(2)0}(I)$ is generated by

$$\langle IM | \mathcal{Y}^{(2)0}(I) | IM \rangle = \sqrt{\left[\frac{5}{I(2I+3)(I+1)(2I-1)}\right]}[I(I+1) - 3M^2]. \tag{40}$$

Consider the two pairs of levels $(M, M+1)$ and $(-M, -M-1)$. The relevant parts of the $(2I+1) \times (2I+1)$ dimensional matrix representation of $\mathcal{Y}^{(2)0}(I)$ are given by two, 2×2 sub-matrices

$$\sqrt{\frac{5}{a_I}}\begin{pmatrix} I(I+1) - 3(M+1)^2 & 0 \\ 0 & I(I+1) - 3M^2 \end{pmatrix}$$

and

$$\sqrt{\frac{5}{a_I}}\begin{pmatrix} I(I+1) - 3M^2 & 0 \\ 0 & I(I+1) - 3(M+1)^2 \end{pmatrix}$$

which can be rewritten as

$$\sqrt{\frac{5}{a_I}}\begin{pmatrix} M_1 - M_2 & 0 \\ 0 & M_1 + M_2 \end{pmatrix} = \sqrt{\frac{5}{a_I}}M_1\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \sqrt{\frac{5}{a_I}}M_2\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{41}$$

and

$$\sqrt{\frac{5}{a_I}}\begin{pmatrix} M_1 + M_2 & 0 \\ 0 & M_1 - M_2 \end{pmatrix} = \sqrt{\frac{5}{a_I}}M_1\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sqrt{\frac{5}{a_I}}M_2\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{42}$$

where

$$M_1 = \tfrac{1}{2}[2I(I+1) - 3(M+1)^2 - 3M^2],$$
$$M_2 = \tfrac{3}{2}(2M+1)$$
and
$$a_I = I(2I+3)(I+1)(2I-1)$$

thereby giving rise to the z component of two Pauli spin-1/2 matrices and an identity matrix. A pulse at resonance with the transition between $\pm M \rightarrow \pm(M+1)$ levels simply rotates the extracted 2×2 submatrices. The decomposition and extraction of Pauli spin-1/2 matrices from any of the $(2I+1) \times (2I+1)$ matrix representing an operator of spin I is rigorously valid since the group $SO(3)$ can be generated from $SU(2)$.

5. Two- and three-pulse expressions for spin 1 and spin 3/2

In the previous section, the results for a single RF pulse applied to a system of quadrupolar nuclei in the absence of a magnetic field were given. It is extended in this section to include a two- and a three-pulse scheme. The extension is considered again with $I = 1$ and $I = 3/2$ as illustrative examples. The expressions for spin 3/2 can be reduced to those of Reddy and Narasimhan under resonance conditions and phase angles used by them.

Starting from (34), the full spin-3/2 density matrix can be decomposed in terms of Pauli spin-1/2 matrices for the component operators $\mathcal{Y}^{(1)1}(1/2)$, $\mathcal{Y}^{(1)0}(1/2)$ and $\mathcal{Y}^{(1)-1}(1/2)$ as

$$
\begin{aligned}
\sigma_{3/2}(t_1^p + t_1) = \tfrac{1}{4}\Bigg[E_{3/2} + i\phi_0^{(2)}(0)\Bigg\{ &\cos\beta_1 \begin{pmatrix} i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix} \\
&+ \frac{i}{\sqrt{2}} \sin\beta_1 \exp\left(i\omega_M^0(t_1^p + t_1) - i\phi_1\right) \begin{pmatrix} i\sqrt{2}\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix} \\
&- \frac{i}{\sqrt{2}} \sin\beta_1 \exp\left(-i\omega_M^0(t_1^p + t_1) + i\phi_1\right) \begin{pmatrix} i\sqrt{2}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix} \\
&- \cos\beta_1 \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{pmatrix} \\
&- \frac{i}{\sqrt{2}} \sin\beta_1 \exp\left(-i\omega_M^0(t_1^p + t_1) + i\phi_1\right) \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & -i\sqrt{2}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \end{pmatrix} \\
&- \frac{i}{\sqrt{2}} \sin\beta_1 \exp\left(i\omega_M^0(t_1^p + t_1) - i\phi_1\right) \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & i\sqrt{2}\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \end{pmatrix} \Bigg\}\Bigg]. \qquad (43)
\end{aligned}
$$

The decomposition of the density matrix as above is to show clearly how the effect of second pulse of phase ϕ_2 and time duration t_2^p may be viewed. The Pauli spin matrices correspond to those of equation (8) for both rotating *and* counter-rotating frames, and the coefficient in front of each matrix in expression (43) is identified to be a $\phi_q^{\pm}$, $q = 1, 0, -1$. The rotation of the component matrices gives equations (18–20) where $\beta = \omega_{1,\text{eff}} t_2^p = \beta_2$, $\phi = \phi_2$ and $\alpha^{\pm} = -\pi/2$ for the present case. Free evolution for a time t_2 after the pulse, changes the off-diagonal elements of the density matrix after the second pulse in the same manner as one would obtain equation (29) from (27). Thus, the density matrix after the evolution period t_2 becomes

$$
\begin{aligned}
\sigma_{3/2}(t_1^p + t_1 + t_2^p + t_2) = \tfrac{1}{4}\Bigg[E_{3/2} + i\phi_0^{(2)}(0)\Bigg\{ & \cos\beta_1 \begin{pmatrix} [M_0^+] & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \end{pmatrix} \\
& + \frac{i}{\sqrt{2}}\sin\beta_1 \exp\left(i\omega_M^0(t_1^p + t_1) - i\phi_1\right) \begin{pmatrix} [M_1^+] & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \end{pmatrix} \\
& + \frac{i}{\sqrt{2}}\sin\beta_1 \exp\left(-i\omega_M^0(t_1^p + t_1) + i\phi_1\right) \begin{pmatrix} [M_{-1}^+] & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \end{pmatrix} \\
& - \cos\beta_1 \begin{pmatrix} \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & [M_0^-] \end{pmatrix} \\
& - \frac{i}{\sqrt{2}}\sin\beta_1 \exp\left(-i\omega_M^0(t_1^p + t_1) + i\phi_1\right) \begin{pmatrix} \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & [M_1^-] \end{pmatrix} \\
& - \frac{i}{\sqrt{2}}\sin\beta_1 \exp\left(i\omega_M^0(t_1^p + t_1) - i\phi_1\right) \begin{pmatrix} \begin{matrix}0&0\\0&0\end{matrix} & \begin{matrix}0&0\\0&0\end{matrix} \\ \begin{matrix}0&0\\0&0\end{matrix} & [M_{-1}^-] \end{pmatrix} \Bigg\}\Bigg]
\end{aligned}
\tag{44}
$$

where

$$
M_q^{\pm} \equiv M_q^{\pm}\left[-\frac{\pi}{2}, \beta_2, \phi_2, \omega_M^0(t_2^p + t_2)\right].
$$

The result in equation (44) has been written down almost without any calculation. The effect of the pulse is thus quite transparent, apart from exponential factors involving t_2, in the process (43) $\rightarrow$ (44). This transformation is central to our picture of what a pulse is in NQR spectroscopy. The calculation of a response to the second pulse is also general compared with that of a single pulse in that one needs all of the six component matrices given by equations (18–20). The density matrix after the second evolution period may be simplified by collecting the terms in equation (44) as

$$\sigma_{3/2}(t_1^p + t_1 + t_2^p + t_2) = \frac{1}{4}\left[E_{3/2} + \phi_0^{(2)}(0)\begin{pmatrix} \sigma_{11} & \sigma_{12} & 0 & 0 \\ \sigma_{12}^* & -\sigma_{11} & 0 & 0 \\ 0 & 0 & -\sigma_{11} & \sigma_{12}^* \\ 0 & 0 & \sigma_{12} & \sigma_{11} \end{pmatrix}\right], \quad (45)$$

where

$$\sigma_{11} = -\cos\beta_1\cos\beta_2 + \sin\beta_1\sin\beta_2\cos\{\omega_M^0(t_1^p + t_1) - (\phi_1 - \phi_2)\}$$

and

$$\begin{aligned}\sigma_{12} = {} & i\cos\beta_1\sin\beta_2\exp\{i\omega_M^0(t_2^p + t_2) - i\phi_2\} \\ & + \frac{i}{2}\sin\beta_1(1+\cos\beta_2)\exp\{i\omega_M^0(t_1^p + t_1 + t_2^p + t_2) - i\phi_1\} \\ & - \frac{i}{2}\sin\beta_1(1-\cos\beta_2)\exp\{-i\omega_M^0(t_1^p + t_1 - t_2^p - t_2) - i(2\phi_2 - \phi_1)\}.\end{aligned}$$

At this stage, the FID can be calculated or equation (45) can be used as the starting point to calculate the effect due to a third pulse. The FID is obtained using equations (30), (35) and (37) as

$$\begin{aligned}\phi_1^{(1)}(t_1^p + t_1 + t_2^p + t_2) = {} & -\frac{i\phi_0^{(2)}(0)}{4}\sqrt{\frac{6}{5}}(\sigma_{12}^* + \sigma_{12}) \\ = {} & -i\sqrt{\frac{3}{40}}\phi_0^{(2)}(0)[2\cos\beta_1\sin\beta_2\sin\{\omega_Q(t_2^p + t_2) + \phi_2\} \\ & + \sin\beta_1(1+\cos\beta_2)\sin\{\omega_Q(t_1^p + t_1 + t_2^p + t_2) + \phi_1\} \\ & + \sin\beta_1(1-\cos\beta_2)\sin\{\omega_Q(t_1^p + t_1 - t_2^p - t_2) - (2\phi_2 - \phi_1)\}].\end{aligned} \quad (46)$$

This is the same as the result given by Reddy and Narasimhan in equation (30) of reference [29*a*] with the following substitutions,

$$\beta_1 = \sqrt{3}\omega_1 t_1^p = \beta_2 = \sqrt{3}\omega_1 t_2^p = \xi, \qquad t_1^p + t_1 \approx t_1 = \tau,$$
$$t_2^p + t_2 \approx t_2 = t - \tau, \qquad \omega_Q = \Delta\omega \text{ and } \phi_1 = \phi_2 = 90°.$$

The effect of a third pulse is now calculated in an identical manner to that of the second pulse. The density matrix following an evolution period t_3 can be given as

$$\sigma_{3/2}(t_1^p + t_1 + t_2^p + t_2 + t_3^p + t_3) = \frac{1}{4}\left[E_{3/2} + \phi_0^{(2)}(0)\begin{pmatrix} \sigma'_{11} & \sigma'_{12} & 0 & 0 \\ \sigma'^*_{12} & -\sigma'_{11} & 0 & 0 \\ 0 & 0 & -\sigma'_{11} & \sigma'^*_{12} \\ 0 & 0 & \sigma'_{12} & \sigma'_{11} \end{pmatrix}\right], \quad (47)$$

where σ'_{11} and σ'_{12} are given in table 1. The FID after 3 pulses and evolution is given

Table 1. Density matrix elements in equation (47).

σ'_{11}	$-\cos\beta_1\cos\beta_2\cos\beta_3$
	$+\frac{1}{2}\sin\beta_1\sin\beta_2\cos\beta_3\exp\{i\omega_Q(t_1^p+t_1)+i(\phi_1-\phi_2)\}$
	$+\frac{1}{2}\sin\beta_1\sin\beta_2\cos\beta_3\exp\{-i\omega_Q(t_1^p+t_1)-i(\phi_1-\phi_2)\}$
	$+\frac{1}{2}\cos\beta_1\sin\beta_2\sin\beta_3\exp\{i\omega_Q(t_2^p+t_2)+i(\phi_2-\phi_3)\}$
	$+\frac{1}{4}\sin\beta_1(1+\cos\beta_2)\sin\beta_3\exp\{i\omega_Q(t_1^p+t_1+t_2^p+t_2)+i(\phi_1-\phi_3)\}$
	$-\frac{1}{4}\sin\beta_1(1-\cos\beta_2)\sin\beta_3\exp\{i\omega_Q(t_1^p+t_1-t_2^p-t_2)+i(\phi_1-2\phi_2+\phi_3)\}$
	$+\frac{1}{2}\cos\beta_1\sin\beta_2\sin\beta_3\exp\{-i\omega_Q(t_2^p+t_2)-i(\phi_2-\phi_3)\}$
	$+\frac{1}{4}\sin\beta_1(1+\cos\beta_2)\sin\beta_3\exp\{-i\omega_Q(t_1^p+t_1+t_2^p+t_2)-i(\phi_1-\phi_3)\}$
	$-\frac{1}{4}\sin\beta_1(1-\cos\beta_2)\sin\beta_3\exp\{-i\omega_Q(t_1^p+t_1-t_2^p-t_2)-i(\phi_1-2\phi_2+\phi_3)\}$
σ'_{12}	$i\cos\beta_1\cos\beta_2\sin\beta_3\exp\{-i\omega_Q(t_3^p+t_3)-i\phi_3\}$
	$-\frac{i}{2}\sin\beta_1\sin\beta_2\sin\beta_3\exp\{-i\omega_Q(t_1^p+t_1+t_3^p+t_3)-i(\phi_1-\phi_2+\phi_3)\}$
	$-\frac{i}{2}\sin\beta_1\sin\beta_2\sin\beta_3\exp\{i\omega_Q(t_1^p+t_1-t_3^p-t_3)+i(\phi_1-\phi_2-\phi_3)\}$
	$+\frac{i}{2}\cos\beta_1\sin\beta_2(1+\cos\beta_3)\exp\{-i\omega_Q(t_2^p+t_2+t_3^p+t_3)-i\phi_2\}$
	$+\frac{i}{4}\sin\beta_1(1+\cos\beta_2)(1+\cos\beta_3)\exp\{-i\omega_Q(t_1^p+t_1+t_2^p+t_2+t_3^p+t_3)-i\phi_1\}$
	$-\frac{i}{4}\sin\beta_1(1-\cos\beta_2)(1+\cos\beta_3)$
	$\times\exp\{i\omega_Q(t_1^p+t_1-t_2^p-t_2-t_3^p-t_3)+i(\phi_1-2\phi_2)\}$
	$-\frac{i}{2}\cos\beta_1\sin\beta_2(1-\cos\beta_3)\exp\{i\omega_Q(t_2^p+t_2-t_3^p-t_3)+i(\phi_2-2\phi_3)\}$
	$-\frac{i}{4}\sin\beta_1(1+\cos\beta_2)(1-\cos\beta_3)$
	$\times\exp\{i\omega_Q(t_1^p+t_1+t_2^p+t_2-t_3^p-t_3)+i(\phi_1-2\phi_3)\}$
	$+\frac{i}{4}\sin\beta_1(1-\cos\beta_2)(1-\cos\beta_3)$
	$\times\exp\{-i\omega_Q(t_1^p+t_1-t_2^p-t_2+t_3^p+t_3)-i(\phi_1-2\phi_2+2\phi_3)\}$

by

$$
\begin{aligned}
\langle I_x\rangle = \frac{\sqrt{3}}{4}\phi_0^{(2)}(0)[&2\cos\beta_1\cos\beta_2\sin\beta_3\sin\{\omega_Q(t_3^p+t_3)+\phi_3\}\\
&-\sin\beta_1\sin\beta_2\sin\beta_3\sin\{\omega_Q(t_3^p+t_3+t_1^p+t_1)+(\phi_1-\phi_2+\phi_3)\}\\
&+\sin\beta_1\sin\beta_2\sin\beta_3\sin\{\omega_Q(t_1^p+t_1-t_3^p-t_3)+(\phi_1-\phi_2-\phi_3)\}\\
&+\cos\beta_1\sin\beta_2(1+\cos\beta_3)\sin\{\omega_Q(t_2^p+t_2+t_3^p+t_3)+\phi_2\}
\end{aligned}
$$

$$+\tfrac{1}{2}\sin\beta_1(1+\cos\beta_2)(1+\cos\beta_3)\sin\{\omega_Q(t_1^p+t_1+t_2^p+t_2+t_3^p+t_3)+\phi_1\}$$
$$+\tfrac{1}{2}\sin\beta_1(1-\cos\beta_2)(1+\cos\beta_3)$$
$$\times\sin\{\omega_Q(t_1^p+t_1-t_2^p-t_2-t_3^p-t_3)+(\phi_1-2\phi_2)\}$$
$$+\cos\beta_1\sin\beta_2(1-\cos\beta_3)\sin\{\omega_Q(t_2^p+t_2-t_3^p-t_3)+(\phi_2-2\phi_3)\}$$
$$+\tfrac{1}{2}\sin\beta_1(1+\cos\beta_2)(1-\cos\beta_3)$$
$$\times\sin\{\omega_Q(t_1^p+t_1+t_2^p+t_2-t_3^p-t_3)+(\phi_1-2\phi_3)\}$$
$$+\tfrac{1}{2}\sin\beta_1(1-\cos\beta_2)(1-\cos\beta_3)$$
$$\times\sin\{\omega_Q(t_1^p+t_1-t_2^p-t_2+t_3^p+t_3)+(\phi_1-2\phi_2+2\phi_3)\}]. \quad (48)$$

This result can also be reduced to equation (43) of Reddy and Narasimhan [29*a*] in the limit of the asymmetry parameter $\eta = 0$ and the following substitutions

$$\beta_1=\beta_2=\beta_3=\xi,\quad t_1^p+t_1\approx t_1=\tau, t_2^p+t_2\approx t_2=T-\tau,$$
$$t_3^p+t_3\approx t_3=t-T,\quad \phi_1=\phi_2=\phi_3=90^\circ \text{ and } \omega_Q=\Delta\omega.$$

The inclusion of the asymmetry parameter in the treatment by Reddy and Narasimhan does not introduce any additional echoes or evolutions in their expressions. This is because η is introduced in first order, which leaves the eigenfunctions of the quadrupole Hamiltonian unchanged but perturbs the frequencies. In many cases, however, η is large enough to be treated more accurately. This means that during the evolution period one must use the eigenfunctions of the full quadrupolar Hamiltonian. This can be done analytically for $I \leq 5/2$ at least.

The expression for $\langle I_x \rangle$ following a three-pulse sequence has not been published for spin 1. We note that it is identical to equation (48) except for the numerical prefactor for an axially symmetric quadrupole. The number of the echoes predicted and their positions are the same as spin 3/2 simply because both $I = 1$ and $I = 3/2$ have only one frequency.

6. Conclusion

NQR multiple pulse experiments are very rich, enabling one to consider a variety of features. Zero-field, $\eta = 0$ cases are the simplest among pulse experiments and our purpose in this paper is to consider the simplest case to present a new way of calculating the response to pulses. Our treatment of an NQR system, and the effect of RF pulses, includes both oppositely rotating components of the RF field, in contradistinction to the NMR system. One component causes a transition $M \rightarrow M+1$ while the other causes a transition $-M \rightarrow -(M+1)$.

Envisioned here are two pulses which excite two simultaneous frequencies of opposite sign. Also, a double resonance experiment in which two different RF fields which are simultaneously resonant with two natural frequencies can be analysed. A small static magnetic field which lifts the degeneracies of the levels can also be treated, since the resonance condition will be violated and off-resonant forms of the matrices $M_q^{\pm}$ will be necessary as given in equations (18–20). An exact treatment of the effect of arbitrary asymmetry (and small magnetic fields orientated along the principal axis) is feasible for $I \leq 5/2$. In every one of these cases, for *all* spin magnitude I, we merely need to use the six 2×2 matrices given by equations (18–20) for analysing pulses. This is a considerable simplification over previous treatments. In any calculation of multiple pulse effects, the algebraic expressions eventually become long and tedious. Reddy and Narasimhan's treatment uses the results of Bowden *et al.* which are based on the use of a spherical tensor operator basis. An immediate difficulty associated with such a basis is that it is *not* a diagonal basis for the dominant quadrupolar interaction (also, the most important one in zero- or low-field NQR). In addition, there is the need for tables of evolution of these operators for each case of differing spin mangitude, which become more involved the higher the spin magnitude. In contrast, the treatment here is applicable to any spin I with only the six 2×2 matrices given by equations (18–20).

In the presence of a large static magnetic field, the spin quantum number (half-integer or integer) is irrelevant in a pseudo two-level description. In NQR spectroscopy, however, the energy level picture may depend on whether we consider half-integer or integer spins. In the presence of a non-axially symmetric electric quadrupole, and in the absence of a static magnetic field, the double degeneracy of the energy levels is lifted only in the integer case. This results in the two components of the RF field having different effects on the pairs of levels among which they cause transitions. In contrast, in the case of half integer spins, both components are either resonant or off-resonant. For the sake of clarity, we did not discuss these differences due to axially asymmetric quadrupolar interactions.

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