Theory of NQR Pulses*

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Pulses applied to spin systems with $I > 1/2$ in the absence of any external fields, the NQR case, are fundamentally different from NMR pulses. In particular, both rotating and counter-rotating components of the rf field must be kept in NQR, whereas only the “in phase” component need be retained in NMR. NQR pulses are illustrated for $I = 3/2$ in an axially symmetric electric field gradient (EFG).

Key words: NQR; Pulse; Density matrix; NMR.

Introduction

In NQR it is customary to refer to a pulse that maximizes the signal as a “90 degree pulse”. In the absence of an external magnetic field and for an axially symmetric EFG there is no direction from which the angle of a pulse can be referenced. NQR differs from NMR in this fundamental way as indicated in Figure 1. The purpose of this paper is to study pulses in NQR and to compare and contrast the effects with the well known NMR cases. Previous work on this subject forms a basis for the approximation used [1–7], with [7] coming the closest to our method [8]. In addition, similar cases have been treated by Reddy and Narasimhan [9] and explicit comparisons are made with their results.

In all treatments it has been recognized that spin systems involving coherences are best described by a spin density matrix, $\rho$, and the time dependence is given by

$$i\hbar \frac{\partial \rho}{\partial t} = \mathcal{L} \rho - iR\rho, \quad (1)$$

where the spin dynamics is described by the Liouville operator and a relaxation term $R$. Since the pulses are of short duration, we assume that relaxation effects are negligible and drop the corresponding term in (1).

The goal of this paper is to describe a series of pulses in the simple case of integer and half-integer spins subject to an axially symmetric quadrupole interaction.

To contrast with NMR, the external magnetic field defines a z-axis about which nuclear spins can align producing a magnetization vector. A pulse of $\theta$ degrees about an axis, say $x$, denoted by $\theta_x$, simply rotates the magnetization around the $x$ axis so the resonant components lie in the $yz$ plane at an angle $\theta$ relative to the z-axis.

![Fig. 1. Contrasting an NMR resonant 90° pulse with the NQR case. What does a pulse do to a spin system, $I > 1/2$, when no external field is present?](image-url)
Figure 2 compares the NMR and NQR situations. The important point to notice is that for NMR, a "hard" pulse is non-selective and all transitions have \( \Delta M = +1 \). In NQR a pulse produces both \( \Delta M = +1 \) and \( \Delta M = -1 \) transitions and is selective.

In both NMR and NQR the rf Hamiltonian is given by

\[
\mathcal{H}_2 / \hbar = \omega_0 I_z + 2 \omega_1 I_x \cos (\omega t - \phi),
\]

which can be rewritten to give

\[
\mathcal{H}_2 / \hbar = + \omega_0 I_z + \omega_1 [I_x \cos (\omega t - \phi) - I_y \sin (\omega t - \phi)] \\
\text{rotating} \\
= + \omega_1 [I_x \cos (\omega t - \phi) + I_y \sin (\omega t - \phi)].
\]

\( couter-rotating \)

Here \( \omega_0 \) is the Larmor frequency and \( \omega_1 \), \( \omega \), and \( \phi \) are the amplitude, carrier frequency and phase, respectively, of the pulse. We refer to the second term in (3) as the rotating component of the rf field and the third as the counter-rotating component.

In the NMR case, if the Larmor precession is rotating in the same sense as the rotating component of the rf field, then this component is close to or on-resonance and causes \( \Delta M = +1 \) transitions, while the counter-rotating component is out-of-resonance by about \( 2\omega \). In NMR, this term is dropped since it causes, under usual experimental conditions, only small Bloch-Siegert shifts. Figure 3 depicts the effects of both components of the rf field in the NMR case. Pure or hard pulses sufficient for most NMR cases have an rf Hamiltonian given by [10],

\[
\mathcal{H}_2 / \hbar = \omega_0 I_z + \omega_1 [I_x \cos (\omega t - \phi) - I_y \sin (\omega t - \phi)].
\]

The NQR case, from Fig. 2, requires both the rotating component of the rf field to produce the \( \Delta M = +1 \) transition and the counter-rotating component to produce the \( \Delta M = -1 \) transition. Like in NMR, the components rotating at \( \pm 2\omega \), out-of-resonance from the \( \Delta M = \pm 1 \) transition frequencies, are ignored. Unlike NMR, an NQR transition is selective. For example the transitions between \( \pm 1/2 \rightarrow \mp 1/2 \) levels are not excited in NQR while they are in NMR (see Fig-
The rf Hamiltonian for NQR is given by the sum of two components $\mathcal{H}_{rf}^+$ and $\mathcal{H}_{rf}^-$, where

$$\mathcal{H}_{rf}^+ = \omega_0^{\text{rf}} [I_x \cos (\omega t - \phi) - I_y \sin (\omega t - \phi)]$$

is the rotating component and

$$\mathcal{H}_{rf}^- = \omega_0^{\text{rf}} [I_x \cos (\omega t - \phi) + I_y \sin (\omega t - \phi)]$$

is the counter-rotating component.

Projecting Composite Spin

Within the above model, the rf Hamiltonian acts on an adjacent pair of levels and causes selective single quantum transitions of $\pm 1$. It is possible to project out the pairs of relevant levels. Figures 4a, b show pictorially how this can be done for integer and half-integer spins. Such projected pairs of levels are fully described by a set of $2 \times 2$ matrices which are the Pauli spin matrices.

Another way to visualize this process is to take a matrix representation of a spin operator and extract the relevant parts. Consider the quadrupole of a spin $5/2$. It's matrix representation is given by [10]

$$Y^{(2)}(I) = \frac{1}{\sqrt{14}} \begin{pmatrix} -5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{pmatrix}. \quad (7)$$
Suppose the transitions from $\pm 1/2 \rightarrow \pm 3/2$ are excited. We simply rewrite the matrix as

$$Y^{(2)0}(I) = \frac{1}{\sqrt{14}} \begin{pmatrix} -5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -5 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$(8)

The first matrix in (8) is not affected by the $\mathcal{H}_\alpha^+$. The second matrix is excited by $\mathcal{H}_\alpha^+$ and the third is excited by $\mathcal{H}_\alpha^-$. The effects of $\mathcal{H}_\alpha^\pm$ are calculated on the appropriate matrices, and the results then recombined into one matrix again.

Another way to visualize this method is to treat the last two matrices in (8) as spin 1/2 vectors. Hence in the above example two composite vectors are extracted as shown in Figure 5.

### Calculation of the Pulse Effects

The effect of an rf pulse on a spin 1/2 is well known [11]. We simply state the results.

First note that the effect of applying $\mathcal{H}_\alpha^\pm$ can be obtained from the $\mathcal{H}_\alpha^\pm$ result by virtue of the symmetry

$$\mathcal{H}_\alpha^+ \rightarrow \mathcal{H}_\alpha^- \quad \text{as} \quad \omega_1 \rightarrow -\omega_1, \quad \omega \rightarrow -\omega \quad \text{and} \quad \phi \rightarrow -\phi.$$ (9)

The density operator for the $2 \times 2$ problem is

$$q_{\pm}(t) = \frac{1}{2} \left[ E_{1/2} + \sum_{q=-1}^{1} Y^{(1)q}(1/2) \phi_q^\pm(t) \right], \quad (10)$$

where the three components $\phi_q^\pm(t)$ denote the vector polarizations of these composite spins with

$$\phi_0^+(t) \sim M_z, \quad \phi_\pm^+(t) \sim M_x \pm i M_y. \quad (11)$$

The spherical tensor operators are given by

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

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

$$Y^{(1)-1}(1/2) = i \sqrt{2} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (12)$$

In terms of Wigner rotation matrices $D^{(1)}_{q\ell}(x, y, z)$ [11] one has

$$\phi_q^\pm(t) = \sum_{q'=-1}^{1} D^{(1)}_{qq'}(x^\pm \theta, \beta, \alpha^\pm \phi + \pi) \phi_{q'}(0), \quad (13)$$

where

$$x^\pm = \mp \tan^{-1} \left[ \frac{\Delta \omega}{\Omega} \tan \left( \frac{\Omega t}{2} \right) \right] - \frac{\pi}{2}, \quad (14)$$

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

$$\Omega = \sqrt{\Delta \omega^2 + \omega_{1,\text{eff}}^2}, \quad \Delta \omega = \omega - \omega^0_M, \quad \omega_{1,\text{eff}}^0 = \sqrt{(I + M)(I - M + 1)} \omega_1 \quad (15)$$

for a transition $M \rightarrow M - 1$. $\omega^0_M$ is defined in Figure 4a. Hence from an initial condition $\phi_q^\pm(0)$ the effect of a pulse on these two pairs of levels is given by

$$q_{1/2}^\pm(t) = \frac{1}{2} \left[ E_{1/2} + \sum_{q'= -1}^{1} \phi_{q'}^\pm(0) M_{q'}^\mp(x^\pm, \beta, \phi, \omega t) \right]. \quad (18)$$

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Fig. 5. a) Vector example of extraction of two composite spins of 1/2 from a quadrupole. b) effect of a pulse on the two extracted spins, c) alternate representation of the effect of a pulse. Note in b) and c) that the composite spins rotate in opposite senses.
where the $M_q^\pm$'s are given by

\[
M_q^\pm (\alpha, \beta, \phi, \omega t) = \begin{pmatrix}
    i \cos \beta & i \sin \beta \exp [i (\alpha^\pm + \phi \mp \omega t)] \\
    i \sin \beta \exp [-i (\alpha^\pm + \phi + \omega t)] & -i \cos \beta
\end{pmatrix},
\]

(19)

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

(20)

and

\[
M_q^- (\alpha, \beta, \phi, \omega t) = \begin{pmatrix}
    +\frac{i}{\sqrt{2}} \sin \beta \exp [-i (\alpha^\pm + \phi)] & \frac{i}{\sqrt{2}} (1 - \cos \beta) \exp [i (2 \phi - \omega t)] \\
    -\frac{i}{\sqrt{2}} (1 + \cos \beta) \exp [-i (2 \alpha^\pm \pm \omega t)] & -\frac{i}{\sqrt{2}} \sin \beta \exp [-i (\alpha^\pm + \phi)]
\end{pmatrix}. \quad (21)
\]

At resonance $\omega = \omega_0^0$, $\alpha^\pm = -\pi/2$. 

Fig. 6. Effects of pulses showing a) a single selective pulse $\pm M \rightarrow \pm M \pm 1$ for an integer spin, $I$, b) a possible double resonance pulse, c) a pulse on the $0 \rightarrow \pm 1$ levels of an integer spin and d) $\pm 1/2 \rightarrow \pm 3/2$ transitions in a $1/2$ – integer spin.
The result has the following relevance. Within the framework of the model described in the introduction, all NQR pulses are described by six $2 \times 2$ matrices given above. Essentially the rotating and counter-rotating components of the rf field cause selective excitations of oppositely oriented composite spins of $1/2$, created by extracting pairs of levels from the spin manifold. These composite spins vectors are rotated in opposite senses fully described by the six matrices $M^\pm_\alpha (\alpha, \beta, \phi_0, \omega_t)$. Figure 6 illustrates this.

The approximation used in this calculation is equivalent to solving the complete problem by dropping the non-secular terms. One of the consequences apparent from this calculation is that the extracted composite spins of $\frac{1}{2}$ are not affected by the quadrupole coupling. The method here is convenient for separating out the effects of rf and quadrupole evolution during a pulse.

Sample Calculation: $I = 3/2$, one Pulse

In this section a sample calculation is performed on a spin $I = 3/2$ to illustrate the method. A series of pulses separated by free evolution periods is considered. We assume, for simplicity, that no asymmetry of the EFG exists ($r_{ij} = 0$).

The initial spin density operator is given by

$$ q_{3/2}(0) = \frac{1}{4} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} , \quad (22) $$

which can be rewritten as

$$ q_{3/2}(t^\xi_1) = \frac{1}{4} \begin{bmatrix} E_{3/2} + i \phi_0^{(2)}(0) \left( \begin{array}{cccc} i & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right) - \begin{array}{cccc} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right) \end{bmatrix} , \quad (23) $$

Here $E_{3/2}$ is the $4 \times 4$ identity matrix and $\phi_0^{(2)}(0)$ is the magnitude of the initial quadrupole alignment. The matrix in (22) is the representation of a second rank tensor proportional to $Y^{(2)}_{0}$ for $I = 3/2$ [10].

After a pulse on the $\pm 1/2 \rightarrow \pm 3/2$ levels, the density matrix becomes

$$ q_{3/2}(t^\xi_1) = \frac{1}{4} \begin{bmatrix} E_{3/2} + i \phi_0^{(2)}(0) \left( \begin{array}{cccc} (M^{(0)}_0) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & (M^{(0)}_0) \end{array} \right) - \begin{array}{cccc} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right) \end{bmatrix} , \quad (24) $$

where $t^\xi_1$ is the duration of the pulse.

In the first evolution period $t_1$, in the $|IM\rangle \langle IM'|$ basis, the quadrupole Hamiltonian for an axially symmetric EFG is diagonal,

$$ |IM\rangle \langle IM'| (t) = \exp \left( \frac{-3i \omega_Q t}{2I(2I-1)} (M^2 - M'^2) \right) |IM\rangle \langle IM'| (0) \quad (25) $$

which simply introduces a frequency component to (24). For $\eta \neq 0$, if the eigenvalues and eigenvectors are known, after a pulse it is necessary to transform into the basis for which the quadrupole Hamiltonian is diagonal. For simplicity this is not considered here (see, however [12]).

After one pulse and evolution, it is possible to calculate, say, the expectation value of $I_x$ given by

$$ \langle I_x \rangle = \text{Tr} \{ \sigma_{3/2}(t^\xi_1 + t_1) I_x \} \quad (26) $$

to give,

$$ \langle I_x \rangle = \frac{\sqrt{3}}{2} \phi_0^{(2)}(0) \sin \left( \sqrt{3} \omega_t t^\xi_1 \right) \sin \left( \omega_0 (t^\xi_1 + t_1) + \phi_1 \right) . \quad (27) $$

This agrees with the results of Reddy and Narasimhan [9] with the following notational changes: $\phi_0^{(2)}$, $\omega_0 = -\omega_0^0$, $\sqrt{3} \omega_t t^\xi_1 = \xi$, $\phi_1 = 90^\circ$.

By virtue of the sine terms in (27), a pulse which rotates the composite spins of $1/2$ through an angle $\xi$ could be considered to be a $90^\circ$ pulse. However the second sine term in (27) only reaches a maximum for $\omega_0 (t^\xi_1 + t_1) = 90^\circ$ for $\phi_1 = 0$. Hence, following a pulse, the signal is zero and thereafter grows. From Fig. 7 a vector description of the formation of this signal is given. This picture is completely different from a $90^\circ$ pulse in NMR [13]. For this reason one cannot use the same criteria to denote pulse angles between NMR and NQR.
\( I = 3/2, \text{ Second Pulse} \)

Continuing from the density matrix \( \rho_{3/2}(t_1^q + t_1) \) given by

\[
\rho_{3/2}(t_1^q + t_1) = 1/4 \begin{pmatrix}
A & B & 0 & 0 \\
-B^* & -A & 0 & 0 \\
0 & 0 & -A & B \\
0 & 0 & B & A
\end{pmatrix}
\]

(29)

where

\[
A = i \cos \beta_1, \quad \text{(30)}
\]

\[
B = \sin \beta_1 \exp [i \omega_M (t_1^q + t_1) - i \phi] \quad \text{and}
\]

\[
\beta_1 = \sqrt{3} \omega_1 t_1^q, \quad \text{(31)}
\]

it is a simple matter to continue the process by rewriting (29) as [14],

\[
\rho_{3/2}(t_1^q + t_1) = 1/4 \begin{pmatrix}
E_{3/2} + i \phi^{(2)}_0(0) & -iA & iB \sqrt{2} & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix}
\]

\[
+ \frac{iB^*}{\sqrt{2}} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} + iA \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} - \frac{iB^*}{\sqrt{2}} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} \right)
\]

(32)

The effect of a second pulse can be calculated by using the 6 matrices (19–21) to give

\[
\rho_{3/2}(t_1^q + t_1 + t_2^q) = 1/4 \begin{pmatrix}
E_{3/2} + i \phi^{(2)}_0(0) & -iA & iB \sqrt{2} & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix}
\]

\[
+ \frac{iB^*}{\sqrt{2}} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} + iA \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} - \frac{iB^*}{\sqrt{2}} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix} \right)
\]

(33)
which is easily recombined to give, after an evolution for time $t_2$,

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

(34)

where

$$e_{11} = -\cos \beta_1 \cos \beta_2 + \sin \beta_1 \sin \beta_2 \\
- \cos \{\omega_M^n(t_1^i + t_1^1) - (\phi_1 - \phi_2)\}, \quad (35)$$

$$e_{12} = i \cos \beta_1 \sin \beta_2 \exp \{i \omega_M^n(t_1^i + t_2^i) - i \phi_2\} + \frac{i}{2} \sin \beta_1 (1 + \cos \beta_2) \exp \{i \omega_M^n(t_1^i + t_1^1 + t_2^i + t_2) - i \phi_1\} - \frac{i}{2} \sin \beta_1 (1 - \cos \beta_2) \exp \{-i \omega_M^n(t_1^i + t_1^1 + t_2^i + t_2) - i (2 \phi_2 - \phi_1)\}. \quad (36)$$

Again $\langle I_x \rangle$ can be calculated, giving

$$\langle I_x \rangle = \langle I_x(t_1^i + t_1^1 + t_2^i + t_2) \rangle = -\phi_0^{(2)}(0) \sqrt{3} (q_{12}^2 + \theta_{12})$$

$$= \frac{\sqrt{3}}{4} \phi_0^{(2)}(0) \left[ 2 \cos \beta_1 \sin \beta_2 \sin (\omega_Q^n(t_2^i + t_2^2) + \phi_2) + \sin \beta_1 (1 + \cos \beta_2) \sin (\omega_Q^n(t_1^i + t_1^1 + t_2^i + t_2) + \phi_1) + \sin \beta_1 (1 - \cos \beta_2) \sin [(\omega_Q^n(t_1^i + t_1^1 - t_2^1 - t_2^2) - (2 \phi_2 - \phi_1)]. \quad (37)$$

Under the conditions
i) on-resonance $\omega_Q = \Delta \omega = -\omega_M^n$, ii) $t_1^i + t_1^1 = T$, iii) $t_2^i + t_2 = T - T$, iv) $\phi_1 = \phi_2 = 90^\circ$.

Equation (37) reduces to the result of [9].

Effects of $n$ Pulses

Continuing the above process gives the same form as (34), i.e.

$$Q_{3/2}(t_1^i + t_1^1 + t_2^i + t_2 \cdots + t_n^i) = 1/4 \left[ E_{3/2} + \phi_0^{(2)}(0) \right] \begin{pmatrix} e_{11} & e_{12} & 0 & 0 \\ e_{12}^* & -e_{11} & 0 & 0 \\ 0 & 0 & -e_{11} & e_{12}^* \\ 0 & 0 & e_{12} & e_{11} \end{pmatrix},$$

and the matrix elements $e_{11}'$ and $e_{12}'$ are easily obtained, although the expressions become longer as the number of pulses increases.

Summary

An NQR pulse differs from an NMR pulse in that it is selective and both $\Delta M = +1$ and $-1$ transitions occur. This means that both the rotating and counter-rotating components of the rf field must be retained. By approximations equivalent to dropping non-secular parts of the Hamiltonian, a simple method results which is based upon extracting pairs of levels that the pulse excites. These act like composite spins of 1/2 and are rotated by the rf field components. All the spin dynamics of NQR pulses is given by six $2 \times 2$ matrices (19–21).

This approach is illustrated by an application of one and two pulses to a spin 3/2 with in an axially symmetric EFG in the absence of an external magnetic field. The results agree with the results of [9].

Although the simplest interactions are treated here for illustrative purposes, the description for asymmetric EFG's remains the same, but involves more algebra. In addition the application of a small external field, say $H_0 \hat{z}$, can be easily incorporated. Essentially this effect moves the system off-resonance for one or the other rf component so that both components cannot simultaneously be on-resonance.

From Fig. 6 it is clear that this method can be applied to double resonance experiments. Also NQR composite pulses are easily treated.
[14] Equation (43) of [8] has some sign errors. However (34) and (44) are correct.