PULSED NQR: AN EXAMPLE OF SELECTIVE EXCITATION

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INTRODUCTION

In pulsed NMR the use of pure pulses corresponding to δ-functions are found to be preferable since they simply produce rotations of the various polarizations. Whilst in principle such ideal infinitely-short pulses should cover all frequencies, in practice both the pulse duration and frequency range are finite. A theory for selectively pulsed NMR (1,2) has recently been developed (7) to cover those cases in which not all spectral frequencies are simultaneously pulsed. Selective irradiation is particularly pertinent to NQR where the large quadrupolar coupling constant ensure that it is rarely possible to pulse all frequencies simultaneously.

In this paper the NMR theory of selective excitations is used to describe pulsed NQR experiments involving single spins of arbitrary magnitude; the effects of rf pulses will be completely predicted for any initial condition. In particular, it is shown that pure NQR frequencies corresponding to transitions between isolated pairs of levels, as in case of $I = 3/2$ with $3/2 \longleftrightarrow 1/2$, or, $-3/2 \longleftrightarrow -1/2$, are not affected by the quadrupole and that such selective pulses correspond to pure pulses. In contrast, for integer spin there will always be a common level shared by two spectral frequencies (e.g. as in $I = 1$ case with $-1 \longleftrightarrow 0 : 0 \longleftrightarrow 1$). This gives rise to effects from both the rf field and the quadrupole which are no longer purely rotations.

In this paper the advantages of a multiplet formulation of selective pulse theory are outlined starting with the NMR case. The theory is extended to consider applications in NQR.

SELECTIVE EXCITATION IN NMR

The multipole formulation of NMR (ref.3-7) writes the spin density operator (ref.8) in terms of a multipole operator basis which is irreducible under the rotation group. Physically k describes the multipole character and the spherical component, $q = \Delta m$ defines the multiquantum coherences (ref.6). The polarizations are simply the expectation value of the corresponding multipole operator, viz:

$$\phi_q^k(t) = \langle \mathcal{Y}_q^k(I) \rangle = \mathrm{Tr}\{\sigma_I(t) \mathcal{Y}_q^k(I)\} . \tag{1}$$

Such knowledge of the nuclear polarizations completely describes the spin state. The spin density operator $\sigma_I(t)$ can be written in the multipole basis as,

$$\sigma_I(t) = \frac{1}{2I+1} \{ E_I + \sum_{k=1}^{2I} \sum_{q=-k}^{+k} \phi_q^k(t) \, \mathcal{Y}^{kq}(I) \} \tag{2}$$

where the adjoint property, $\mathcal{Y}_q^{k\dagger} \equiv \mathcal{Y}^{kq}$, has been used. The time evolution is determined by the standard form,

$$i\hbar \frac{\partial \sigma_I(t)}{\partial t} = [\mathcal{H}, \sigma_I(t)]_- \tag{3}$$

where $\mathcal{H}$ is the Hamiltonian for the system.

In solving (3), it will be seen that exponentiation of and use of unitary operators of form $U = \exp(-i\mathcal{H}t)$, as in (ref. 13), has been completely avoided. Instead, one commutator is calculated and a set of coupled first order differential equations obtained,

$$i\hbar \frac{d\phi}{dt} = \underline{\underline{\mathcal{L}}} \cdot \underline{\phi} \tag{4}$$

where $\underline{\phi}$ is a vector spanning indices k and q, and $\underline{\underline{\mathcal{L}}}$ has a matrix representation of the form

$$(\underline{\underline{\mathcal{L}}})_{kq,k'q'} = tr\{ \mathcal{Y}^{kq\dagger} [\mathcal{H}, \mathcal{Y}^{k'q'}]_- \} \tag{5}$$

It is clear that the concepts and representations implicit in (4) and (5) are derived in part from earlier ideas (ref. 9) dealing with Liouville operators. It is necessary to specify the initial conditions $\underline{\phi}(0)$ to obtain a solution of (4).

The multipole theory of selective excitation focusses on the multiplet subset of levels irradiated by the pulse. In conventional NMR only single quantum $q = \Delta r_i = \pm 1$ coherences are observed; for NQR these frequencies are the strongest features. For $q = \pm 1$ pairs of adjacent levels may be used to define a multiplet spin of 1/2; the formalism has been discussed elsewhere (ref. 5). When two transitions that share a common level are simultaneously excited within a three level submanifold, the multiplet spin is not 1/2; a multiplet spin of 1 now applies with the level construction illustrated in Fig. 1. Further generalization of the multiplet concept to multiquantum transitions is straight forward.

Such an I_M multiplet spin will act on a $(2I_M+1)$ subspace and allow one to write formal equations (ref. 7) analagous to (1)-(5). The multiplet spin density operator is then

$$\sigma_{I_M}(M) = \frac{1}{2I_M+1} \{ E_{I_M} + \sum_{p=1}^{2I_M} \sum_{q=-p}^{+p} \phi_q^p(I_M M) \, \mathcal{Y}_{I_M}^{pq}(M) \} \tag{6}$$

which is particularly simple for $I_M = 1/2$, or 1. For a Hamiltonian
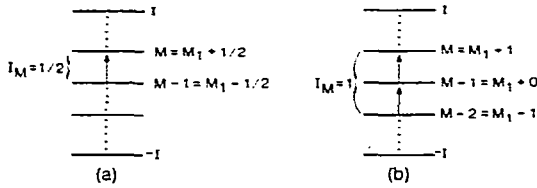
Fig.1. Selective excitation of (a) one transition defining an $I_M = \frac{1}{2}$, and (b) two single quantum transitions defining an $I_M = 1$, multiplet spin.

$$\mathcal{H} = -\gamma \hbar w_o I_z + \frac{\hbar \tilde{Q}}{I(2I-1)} \left\{ 3I_z^2 - I(I+1) \right\} - \hbar I_x \omega_1 \cos(\omega t - \phi) + \hbar I_y \omega_1 \sin(\omega t - \phi) \tag{7}$$

where ϕ is the phase angle and $\omega_o = \gamma H_o$, it is found that for the single quantum selective excitation, the rf amplitude is replaced (ref.3,10) by

$$\omega_{1,eff} = \sqrt{(I+m)(I-m+1)} \; \omega_1 \tag{8}$$

and the quadrupole term $\tilde{Q}$ is replaced by $\tilde{Q}_{eff}$(ref.3). For $I_M = 1/2$, $\tilde{Q}_{eff} = 0$ and for $I_M = 1$ the effective term is

$$\tilde{Q}_{eff} = \frac{2\tilde{Q}}{I(2I-1)} \tag{9}$$

It is significant that for multiplet spins $I_M = 1/2$, regardless of the magnitude of $\tilde{Q}$, the effect of an rf pulse is solely determined by the rf Zeeman term. The result is a pure rotation (ref.6,7),

$$\hat{\phi}_q^1 (\tfrac{1}{2}M) [(\alpha\beta)_\phi] = \sum_{q'} \mathcal{D}_{qq'}^{(1)} (-(\phi-\alpha), \beta, (\phi-\alpha)) \phi_{q'}^1 (\tfrac{1}{2}M)(0) \tag{10}$$

The angles α and β are given for both on and off-resonance conditions (ref.6); in the present context, ω_1 is replaced by $\omega_{1,eff}$. It is seen that (8) is the origin of the $\sqrt{3}\omega_1$, and $2\omega_1$ factors found in selective processes (ref.10,11); these may be interpreted physically as increases in γ and the effective rf power arising from localization of the rf to the $I_M < I$, $(2I_M+1)$ subspace, rather than being spread over $(2I+1)$ levels as in the non-selective case. In (10) the Wigner rotation matrices are defined with use of the convention of Edmonds (ref.12) and $\hat{\phi}_q^1$ implies the rotating frame defined by $\hat{\phi}_q^k = e^{-iq \omega_o t} \phi_q^k$.

For a selective pulse acting on a multiplet spin $I_M = 1$, the combination of both rf and quadrupole interactions must be considered. This has been solved by

perturbation theory (ref.3) in the limits $|\omega_{1,eff}| > |\tilde{Q}_{eff}|$. Since the effective rf amplitude is larger than ω_1 whilst the effective quadrupole coupling constant is less than $\tilde{Q}$, clearly the limit $|\omega_1| > |\tilde{Q}|$ is particularly easily satisfied by selective pulses. The result is,

$$\phi_q^p(I_M M) = \sum_{p'\tilde{q}q'} \mathcal{D}_{q\tilde{q}}^{(p)} (\Delta\omega-\phi,-\theta,0)\exp\{iQ_{eff}\tilde{q}t\} \, M_{\tilde{q}}^{pp'}(t) \mathcal{D}_{\tilde{q}q'}^{(p')}(0,\theta,-\phi)\phi_{q'}^{p'}(I_M M)[0] \quad (11)$$

where

$$Q_{eff} = \sqrt{\Delta\omega^2+\omega_{1,eff}^2} \quad (12)$$

$$\cos\theta = \Delta\omega/Q \quad (13)$$

and where the effective quadrupole occurring in the development matrices $\underline{\underline{M}}(t)$ is given by,

$$\tilde{\tilde{Q}}_{eff} = -\frac{1}{2}\left\{\frac{1-2\Delta\omega^2/\omega_{1,eff}^2}{1+\Delta\omega^2/\omega_{1,eff}^2}\right\}\tilde{Q}_{eff} \quad (14)$$

The forms of the $\underline{\underline{M}}$ matrices for $I < 9/2$ and for $I_M = 1$ have been given elsewhere (ref.6); for single quantum process it is simply,

$$\underline{\underline{M}}(t) = \begin{pmatrix} \cos\tilde{\tilde{Q}}_{eff}t & , & \sin\tilde{\tilde{Q}}_{eff}t \\ -\sin\tilde{\tilde{Q}}_{eff}t & , & \cos\tilde{\tilde{Q}}_{eff}t \end{pmatrix}. \quad (15)$$

Clearly a pure rotation corresponding to case of $I_M = 1/2$ is physically easier to visualize than $I_M = 1$, although in actual use at resonance, $\Delta\omega=0$ (eq.11) simplifies considerably for $I_M=1$.

The treatment outlined here describes single quantum selective excitations within the $2I_M+1$ subset of levels. To be of use, it is necessary to extract the multiplet density operator from the full density matrix operator. This is easily done in NQR problems, expecially when the system is initially at equilibrium.

PULSED NQR

As an example, the case of an axially symmetric quadrupole for $I=3/2$ within a principle axis convention and in the absence of an external field is treated. The equilibrium density matrix operator is

$$\sigma_{3/2}(0) = \frac{1}{4}\{E_{3/2} + \phi_0^2(0)\mathcal{Y}^{20}(I)\} \quad (16)$$

where, as in paper III,

$$E_{3/2} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \sum_{\substack{M,M'= \\ -3/2}}^{3/2} \delta_{MM'} \quad (17) \quad \text{and} \quad \mathcal{Y}^{20} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad (18)$$

The matrix representations refer to the MM' basis (ref.5). Equation (18) is easily decomposed into multiplet spins of 1/2 to give,

$$\sigma_{3/2}(0) = \tfrac{1}{4}\{E_{3/2} - \phi_0^2(0)\,\mathcal{Y}_{1/2}^{10}(3/2) + \phi_0^2(0)\,\mathcal{Y}_{1/2}^{10}(-1/2)\} \qquad (19)$$

The notation $\mathcal{Y}_{1/2}^{10}(M)$ and $\phi_0^1(1/2\ M)$ refer to an $I_M = 1/2$ multiplet spin of two states composed of levels M, the uppermost, and m-1, represented in matrix notation by

$$\mathcal{Y}_{1/2}^{10}(3/2) = \iota \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad (20) \qquad \text{and} \qquad \mathcal{Y}_{1/2}^{10}(-1/2) = \iota \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad (21)$$

From equation (6) it follows that

$$\phi_0^1(\tfrac{1}{2}\ \tfrac{3}{2}) = i\phi_0^2(0) \qquad (22) \qquad \text{and} \qquad \phi_0^1(\tfrac{1}{2}\ \tfrac{-1}{2}) = -i\phi_0^2(0) \qquad (23)$$

An important aspect of this picture is that the two multiplet spins of 1/2 refer to the 3/2 <--> 1/2 transition and the -3/2 <--> -1/2 transition. The degenerate states clearly imply that the multiplet spin $\mathcal{Y}^{10}(1/2\ 1/2)$ is not needed and the -1/2 <--> 1/2 transition is not excited. It is precisely because only two of the three single quantum processes are excited, that the pulse on I = 3/2 at zero field is selective. Eq. (10) describes the effects of a pulse on each multiplet spin 1/2; substituting the results from Eq. 10 into Eq. 19 gives the full density matrix, $\sigma_{3/2}([\alpha\beta]_\phi)$, after the pulse. The only modification required in NQR formalism is the absence of the rotating frame in Eq. (10) derived for NMR from the Zeeman frequency.

Choosing t_w as the duration of the pulse, at resonance with the pure quadrupole frequency ω_o for the +3/2 <--> + 1/2 transition, so that $\Delta\omega=0$ and $\omega=\omega_o$, and invoking Eq. (8) gives

$$\phi_1^1(t_w) = \text{Tr}\{\mathcal{Y}^{11}(I)\sigma_{3/2}(t)\}$$

$$= i\ \sqrt{3/10}\ \phi_0^2\ \sin(\sqrt{3}\omega_1 t_w)\ \sin\omega_o t_w\ e^{i\phi} \qquad (24)$$

Since $\phi_1^1(t_\omega) \propto \langle I_-\rangle$, the two components of ϕ_1^1 correspond to $\langle I_x\rangle$ and $\langle I_y\rangle$ after the pulse. Hence the result is simply

$$\phi_x(t_w) = -\sqrt{3/5}\ \phi_0^2(0)\ \sin(\sqrt{3}\omega_1 t_w)\ \sin\omega_o t_w = 2/\sqrt{5}\ \langle I_x\rangle \qquad (25)$$

for phase angle of $\phi = 0$. This agrees with the expression Eq.(13) calculated in ref.11 with $\phi_0^2(0) = -1$.

CONCLUSION AND GENERALIZATIONS

Provided the irradiation is only perturbing a single resonance, any half-interger spin system can be described by multiplet spins of 1/2; these all have of necessity $\tilde{Q}_{eff}= 0$, even in the presence of large quadrupolar coupling constants. Moreover, the rf amplitude is increased according to (8). It is only necessary to extract the multiplet spins 1/2 from the total spin density operator for spin I, as in (ref.6); use (10) and reinsert the result in the total spin density operator $\sigma_I(t)$. The case of I=3/2 for NMR is treated in III (ref.5).

For integer spins the same treatment holds for all single quantum transitions except the 1 <--> 0 and -1 <--> 0. These two are both coincident in frequency and share common level; therefore the two transitions must be treated by a multiplet spin of $I_M=1$, as in III. In this case $\tilde{Q}_{eff}$ is not zero but is given by (9) and (14). Further, the effect of the pulse is not a pure rotation but rather a combination of quadrupolar and rf evolution that may approximately described by (11) provided $|\omega_{1,eff}| >> |\tilde{Q}_{eff}|$.

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