

Multipole N.M.R.

V. Theory of selective multiquantum excitation

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Using a multipole formalism and the concept of multiplet spin (groups of closest nuclear levels), selective excitation of multiquantum lines is treated. Both pure pulses, no internal coupling, and finite pulses, some internal coupling, are covered. The results, valid for single spins of arbitrary magnitude are compared to the fictitious spin 1/2 approach.

1. INTRODUCTION

Multiquantum spectra in N.M.R. are composed of fewer lines than single quanta spectra [1, 2]. Excitation of polarization of a spin system other than the vector magnetization, allows additional and complimentary data to be extracted which probe the lattice and spin-spin couplings in ways which differ with the tensor rank of the nuclear polarization. The detection of these polarizations is only possible indirectly, that is by transferring them to the magnetic dipole in the xy plane. Two-dimensional spectroscopy [3] has emerged as one technique for studying multiquantum spectra. In solids, the Jeener-Broekaert sequence [4] enables a quadrupole (2nd rank) population distribution to be measured. The WAHUA [5] and related cyclic pulse sequences [6] reduce dipolar coupling in solids while pulse-phase shifting [1, 7] can lead to n -quantum selective excitation [8]. In addition selective or tailored pulses can excite only one part of the multiquantum spectrum leading to a great variety of results [9–15].

Until recently the spin dynamics has been treated almost entirely in the Heisenberg picture and the time dependence of an operator obtained by calculating quantities of the type [12]

$$\mathcal{H}^* = U^\dagger \mathcal{H} U, \quad (1)$$

where U is an evolution operator. Appropriate bases for single spins have been discussed as alternatives to the $|IM\rangle\langle IM'|$ basis, notably for selective excitation, the fictitious spin 1/2 approach [11, 12]. This rests on a tradition of spin calculation used for several decades [16, 17].

On the other hand in order to understand multiquantum processes in N.M.R. it is essential to calculate the quantum mechanical density operator

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[18] which contains information of the various population distributions and multi-quantum coherences (called, collectively, polarizations). In this paper the polarizations are organized into multipoles. The particular operator basis chosen [19], denoted $\mathcal{Y}^{(k)q}(\mathbf{I})$, are q th spherical components of k th rank tensors irreducible under the rotation group [24]. The spherical component, $q = \Delta M$, corresponds to the q th quantum coherence. A given hamiltonian causes the various multipoles to mix so that populations and coherences can be transferred and interchanged. Multipulse N.M.R. can be viewed as creating multipole polarizations and studying how the lattice responds to the presence of these polarizations.

The treatment is restricted to a single spin of arbitrary magnitude with a quadrupole interaction which causes the Zeeman levels to be perturbed. The spread in the spectrum of different frequencies which arises allows specific, selective, irradiation of specific lines. All such selective transitions are assumed to be caused by the spin interacting with an r.f. field oscillating in the xy plane. Two types of selective pulses are treated. Pure selective pulses which are of short duration with respect to the internal couplings, and finite pulses, in which internal couplings can act. The former refers to the case when the internal interaction has split the levels sufficiently to allow selective irradiation of the line, but during the time of irradiation, no appreciable internal couplings occur leading to a description of a pure rotation within the irradiated multiplet. It is shown for single spins with a nuclear quadrupole, that multiplet spins of $1/2$ (nearest doublets) have an effective quadrupole of zero. Single quantum selective excitations, therefore, are always pure in this case. In agreement with others [9, 12] for selective pulses, the effective r.f. strength increases ($\omega_{1, \text{eff}} > \omega_1$). In addition, it is shown that the effective quadrupole coupling constant decreases ($\bar{Q}_{\text{eff}} < \bar{Q}$) thereby reducing internal coupling.

This work rests heavily on previous treatments of (i) the solution of the full density matrix for single spins in a static field with a nuclear quadrupole interaction [20]; (ii) the solution of a single spin in an r.f. field with no interactions (pure pulses) [20–22]; and (iii) the theory of multiplet spin [23]. The last is reviewed in § 2.

The approach here differs considerably with those of Vega and Pines [12] and Wokaun and Ernst [9]. Their treatments, based upon the fictitious spin- $1/2$ formulations have been successfully applied to spins of low magnitude ($I=1, 3/2$). In this paper the general result, valid for any multi-quantum transition for a spin of any magnitude, agrees completely with the fictitious spin- $1/2$ calculations of Wokaun and Ernst [9] when reduced to a selective single quantum transition for a spin 1. For higher multi-quantum selective excitations [9, 12] the limit $\omega_1 \ll \omega_Q$ is invoked. In this limit the results here agree although it is argued in contrast to the usual experimental procedure that the opposite limit $\omega_1 > \omega_Q$ is more easily made selective for $I > 1$ than is the limit $\omega_1 \ll \omega_Q$. In other words, weak, long irradiation ($\omega_1 \ll \omega_Q$) becomes non-selective because internal couplings disperse the radiation into many modes.

Viewed from the multipole formalism, multi-quantum processes are harmonics of single quantum processes. The various multipoles corresponding to the q th quantum process make up the multipole character of the spectrum [20, 23]. In the next section physical motivations for using multipoles are given with emphasis on the effects of selective excitation on the multipole character of the

spectrum. The mathematics of this is treated in § 3 for pure selective pulses while some examples are discussed in § 4. Finite non-selective (§ 5) and finite selective (§ 6) pulses are discussed assuming the pulse is of sufficient duration that the quadrupole can couple.

Not treated here are multispin selective excitations although the mathematics of multispin multipole basis operators exists [19]. Relaxation is assumed negligible while the pulse is on and is omitted. Also the relation to various interactions representations (tilted axes) [12] is not carried out in spite of their usefulness [15]. However the relation between the multipole and fictitious spin-1/2 approach has been given [23].

2. PHYSICAL DESCRIPTION OF SELECTIVE EXCITATION

In order to study multi-quantum processes the spin density matrix is expanded in multipoles [20, 23]

$$\sigma_I(t) = \frac{1}{2I+1} \left[E_I + \sum_{k=1}^{2I} \sum_{q=-k}^k \phi_q^k(t) \mathcal{Y}^{(k)q}(\mathbf{I}) \right]. \quad (2)$$

Knowledge of the $\phi_q^k(t)$, the multipole polarizations, completely determines the spin state. When a single spin with a nuclear quadrupole interaction is in a static field the energy levels are perturbed [20] according to

$$E_{IM} = -\hbar\omega_0 M - \frac{\hbar\tilde{Q}}{2I(2I-1)} [I(I+1) - 3M^2]. \quad (3)$$

The existence of these stationary states does not reveal any spectra. At equilibrium only the magnetization in the z direction is non-zero, being described by ϕ_0^1 with all other ϕ s being negligible.

To illustrate the multipole character of lines [20, 23] for $I=3/2$, the detectable polarization is

$$\begin{aligned} \phi_{\pm 1}^1(t) = \frac{\exp(\pm i\omega_0 t)}{5} [(2 + 3 \cos(\tilde{Q}t))\phi_{\pm 1}^1(0) \pm \sqrt{15} \sin(\tilde{Q}t)\phi_{\pm 1}^2(0) \\ + \sqrt{6}(1 - \cos(\tilde{Q}t))\phi_{\pm 1}^3(0)]. \quad (4) \end{aligned}$$

Although not included, this polarization relaxes in the time domain t giving an FID. Fourier transforming the FID, i.e. (4), gives three lines at ω_0 and $\omega_0 \pm \tilde{Q}$ —the single quantum spectrum. The multipole character of these lines depends upon the past history which creates dipole, $\phi_{\pm 1}^1(0)$; quadrupole, $\phi_{\pm 1}^2(0)$; and/or octupole $\phi_{\pm 1}^3(0)$ character. Figure 1 shows the single quantum spectrum for $I=3/2$. All the multi-quantum spectra can be similarly decomposed.

To illustrate one advantage of selective excitation, suppose an initial unselective $\pi/2$ pulse has created an xy single quantum coherence. This contains only dipole character so its Fourier transform contains three lines as shown in figure 2 (top). Application of a π selective pulse at resonance ω_0 creates pure single quantum octupole character with *no* creation of other polarizations. That is the only non-zero polarization present after the selective pulse is $\phi_{\pm 1}^3$. The Fourier transform of this FID would reveal a pure octupole single quantum spectrum, but a non-selective resonant pulse applied soon after the selective

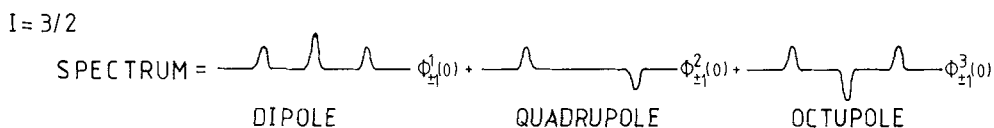


Figure 1. A single quantum spectrum for $I=3/2$ decomposed into its multipole components.

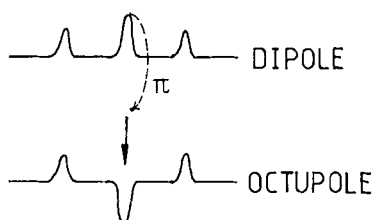


Figure 2. Creation of single quantum octupole polarization from a single quantum dipole polarization by a resonant π selective pulse.

pulse will create zero, triple or double quantum coherences with pure octupole character, according to [20]

$$\phi_q^3([\beta]_{\Phi}) = \exp(iq\omega_0 t) \mathcal{D}_{q\pm 1}^{(3)}(-(\phi_p - \pi/2)\beta(\phi_p - \pi/2)) \phi_{\pm 1}^3(0). \quad (5)$$

Here ϕ_p is the phase angle of the applied r.f. field [20], $\beta = \omega_1 \tau$ is the angle through which the polarization is rotated and $\mathcal{D}_{qq}^{(k)}$ is a rotation matrix [24]. This example shows that unwanted polarizations can be suppressed. Obvious restrictions on this analysis lie in the necessity of having well separated lines such as exist in single crystals or molecules oriented in liquid crystals with negligible spin-spin interactions.

The mathematical description implied in figure 2 is a pure rotation of a specific line. This work discusses how specific multiplet spins can be rotated by selective pulses in analogy with the usual description of pulses on magnetic vectors. This is done by the use of the multiplet spin concept [23]; groups of closest levels in the $2I+1$ manifold. The resulting multiplet spin space can be spanned by operators $\mathcal{Y}_{I_M}^{(p)q}(M)$ which have exactly the same structure and properties of a spin $I=I_M$ except that the representation of $\mathcal{Y}_{I_M}^{(p)q}(M)$ are submatrices of the total spin space. These operators can be used to represent the multiplet spin density operator $\sigma_{I_M}(M)$ defined by [23] (cf. equation (2))

$$\sigma_{I_M}(M) = \frac{1}{2I_M+1} \left[E_{I_M} + \sum_{p=1}^{2I_M} \sum_{q=-p}^p \phi_q^p(I_M M) \mathcal{Y}_{I_M}^{(p)q}(M) \right]. \quad (6)$$

The multiplet spin polarizations are $\phi_q^p(I_M M)$ and the M label indicates that the multiplet spin is composed of the $(2I_M+1)$ levels of which the M th level (of spin I) is the uppermost of I_M (see figure 1 of paper III).

As shown in paper (III), an advantage of the multiplet spin density operator is that it can be extracted from the full density operator σ_I , equation (2). Consequently, when a selective excitation between two separated levels is under study, the appropriate density matrix for the $(2I_M+1)$ multiplet is subtracted from the full density matrix. The effect of the selective excitation is then

calculated for the multiplet spin, and the result is then re-embedded back in the full density matrix.

A single quantum process involves two nearest levels and requires a multiplet spin of 1/2. This case is equivalent to the fictitious spin-1/2 approach for nearest levels. A double quantum process requires 3 nearest levels, and is described by multiplet spin 1; the q th quantum process requires a multiplet spin of magnitude $|q|/2$.

3. PURE SELECTIVE PULSES

In this section the general case is treated, namely an r.f. field is applied at or near a multiquantum transition frequency. It is assumed that the level splittings are unequal, such as arise from (3). Selective excitation occurs when a transition between the M th and $M-q$ level takes place. This refers to a particular line in the q th quantum spectrum of a single spin. Following on from the last section and [23], a multiplet spin and multiplet spin density operator are defined giving equation (6). To calculate the effect of a pulse the full (spin I) hamiltonian is used. Using the properties of the $\mathcal{Y}_{I_M}^{(p)q}(M)$, [23], gives

$$\begin{aligned} \frac{i\hbar \partial \phi_q^p(I_M M)}{\partial t} &= \frac{-\text{Trace}}{(2I_M+1)} \left\{ \sum_{p'q'} [\mathcal{Y}_{I_M}^{(p)q\dagger}(M), \mathcal{Y}_{I_M}^{(p')q'}(M)] \mathcal{H} \phi_q^{p'}(I_M M) \right\} \\ &= 2 \sum_{\substack{p''q'' \\ p'q'}} \phi(p'' p p') \ll \mathcal{Y}_{I_M}^{p''}(M) \parallel \mathcal{Y}_{I_M}^p(M) \parallel \mathcal{Y}_{I_M}^{p'}(M) \gg (-1)^{p-q} \\ &\quad \times \begin{pmatrix} p & p' & p'' \\ -q & q' & q'' \end{pmatrix} \frac{\text{Trace}}{(2I_M+1)} \{ \mathcal{Y}_{I_M}^{p''q''\dagger}(M) \mathcal{H} \} \phi_q^{p'}(I_M M). \end{aligned} \quad (7)$$

Further reduction depends on the form of the hamiltonian. For pure pulses, \mathcal{H} is the Zeeman hamiltonian

$$\begin{aligned} \mathcal{H}(t) &= -\gamma \hbar \mathbf{I} \cdot \mathbf{H}(t) \\ &= -\hbar \gamma \sqrt{[I(I+1)]/3} \sum_{m=-1}^1 H_m(t) \mathcal{Y}_I^{(1)m}, \end{aligned} \quad (8)$$

where

$$H_0 = -iH_z \quad (9)$$

and

$$H_{\pm 1}(t) = \frac{\pm i H_1}{\sqrt{2}} \exp [\pm i(\omega t - \phi_p)]. \quad (10)$$

All terms are defined in [20]. In particular ϕ_p is the phase angle and H_1 and H_0 define frequencies $\omega_0 = \gamma H_z$ and $\omega_1 = \gamma H_1$. However ω_0 does not correspond to the exact energy level splitting because of the nuclear quadrupole term, (3). To correct for this it is assumed that $q\omega_0$ is replaced by

$$\begin{aligned} \hbar q \omega_0 &\rightarrow \hbar q \omega_0 + \hbar \omega_{Mq}^I = E_{IM} - E_{IM+q} \\ &\equiv q \hbar \omega_{0q}^I(M) \end{aligned} \quad (11)$$

using (3).

The calculation with this hamiltonian is carried out using equation (46) of [23]. The basic equations governing the response of the multiplet spin polarizations to an r.f. field are

$$\begin{aligned} \frac{\partial \phi_q^p(I_M M)}{\partial t} = & 2 \sum_{p'q''} \phi(pp'p'') \ll \mathcal{Y}_{I_M}^{p''} \| \mathcal{Y}_{I_M}^p \| \mathcal{Y}_{I_M}^{p'} \gg (-1)^{p-q} \begin{pmatrix} p & p' & p'' \\ -q & q' & q'' \end{pmatrix} \\ & \times \sum_{M M' M''} (i)^{p-1} \left[\frac{(2I+1)}{(2I_M+1)} (2p''+1) \right]^{1/2} (-1)^{I-M+I_M-M''} \\ & \times \begin{pmatrix} I_M & p'' & I_M \\ -M_M & q'' & M'_M \end{pmatrix} \begin{pmatrix} I & 1 & I \\ -M_1+M_M & q'' & M_1-M'_M \end{pmatrix} \\ & \times \sqrt{[I(I+1)]} \left\{ \omega_{0q}^I(M) \delta_{q''0} - \frac{\omega_1 \exp [+i(\omega t - \phi_p)]}{\sqrt{2}} \delta_{q''1} \right. \\ & \left. + \frac{\omega_1}{\sqrt{2}} \exp [-i(\omega t - \phi_p)] \delta_{q''-1} \right\} \phi_q^{p'}(I_M M). \quad (12) \end{aligned}$$

This generates a set of coupled equations for the multiplet spin polarizations $\phi_q^p(I_M M)$. The multiplet spin state is $|I_M M_M\rangle$ and full spin I basis is $|IM\rangle$. M_1 , discussed in [23], is $M = M_1 + M_M$. When $I_M = I$, $M_1 = 0$ and the sum over M_M is possible which reduces to (42) of [20], i.e. the full spin (non-selective) problem.

4. PURE SINGLE QUANTUM SELECTIVE EXCITATION

This case focuses on any adjacent pair of levels which are selectively excited. The multiplet spin 1/2 can have only a dipole (vector) operator $p = 1$. In this case $p = p' = p'' = 1$ in (12) which reduces exactly to

$$\begin{aligned} \frac{\partial \phi_q^1(I_M M)}{\partial t} = & i\omega_{01}^I(M) q \phi_p^1(I_M M) \\ & + \frac{i\omega_{1,\text{eff}}}{\sqrt{2}} \exp [+i(\omega t - \phi_p)] \sqrt{[(1+q)(2-q)]} \phi_{q-1}^1 \\ & + \frac{i\omega_{1,\text{eff}}}{\sqrt{2}} \exp [-i(\omega t - \phi_p)] \sqrt{[(1-q)(2+q)]} \phi_{p+1}^1. \quad (13) \end{aligned}$$

This is identical to (42) of [20] except that ω_1 is replaced by $\omega_{1,\text{eff}}$,

$$\omega_{1,\text{eff}} = \sqrt{[(I+M)(I-M+1)]} \omega_1, \quad (14)$$

meaning that the effect of the r.f. field is stronger when selectively applied to a pair of levels. The magnitude, moreover, can vary with the $M, M-1$ pair of levels excited. For $I=1$, both the $1 \leftrightarrow 0$ and $0 \leftrightarrow -1$ have $\omega_{1,\text{eff}} = \sqrt{2} \omega_1$ which is the same factor found from the fictitious spin theory [11, 13]. For $I=3/2$, the selective effective r.f. magnitudes vary with M .

The solution to equation (13) is found in exactly the same way as in [20]. The result is

$$\hat{\phi}_q^1(I_M M)[(\alpha\beta)_{\phi_p}] = \sum_q \mathcal{D}_{qq'}^{(1)}(-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \phi_q^1(I_M M)[0]. \quad (15)$$

The notation $[\alpha\beta]_{\phi_p}$ refers to the effect of a non-resonant rotation through angles $\alpha\beta$ due to an r.f. field with phase angle ϕ_p . The angles are given by equations

(57)–(60) of [20] with Ω replaced by

$$\Omega_{\text{eff}} = \sqrt{[\Delta\omega^2 + \omega_{1,\text{eff}}^2]}. \tag{16}$$

The frame is rotating at the transition frequency (cf. (11))

$$\hat{\phi}_q^1(I_M M) = \exp[-i(q\omega_0 + \omega_{Mq}^I)t] \phi_q^1(I_M M) \tag{17}$$

and the energy mismatch from the applied r.f. frequency is

$$\Delta\omega = \omega - \omega_0 - \omega_{Mq}^I/q. \tag{18}$$

When $|\Delta\omega| \gg \omega_{1,\text{eff}}$ the r.f. pulse has negligible effect on the multiplet spin (adiabatic limit). Consequently the applied r.f. frequency should be close to the transition frequency. To indicate this $|\Delta\omega| \equiv |\delta\omega| \leq |\omega_{1,\text{eff}}|$ where $\delta\omega$ is a small mismatch.

The results of this section extend previous single quantum treatments to selective pulses on spins of any magnitude from any non-equilibrium prepared state. Also, the interpretation retains the picture of rotation of nuclear polarizations.

5. EXAMPLES OF SELECTIVE SINGLE QUANTUM TRANSITIONS

It is possible to compare the above directly with the treatment by Wokaun and Ernst [11]. The density operator for $I=1$ irradiating the $M=1, 0$ doublet is, from [11], equation (34),

$$\rho(t) = b \begin{pmatrix} \frac{1}{2} + \frac{1}{2}\Lambda_1 & \frac{1}{2}\Lambda_2 & 0 \\ \frac{1}{2}\Lambda_2^* & \frac{1}{2} - \frac{1}{2}\Lambda_1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{19}$$

where

$$\Lambda_1 = \cos^2 \theta + \sin^2 \theta \cos \omega_{\text{eff}}t, \tag{20}$$

$$\Lambda_2 = \frac{1}{2} \sin 2\theta(1 - \cos \omega_{\text{eff}}t) + i \sin \theta \sin \omega_{\text{eff}}t \tag{21}$$

$$\omega_{\text{eff}} = \sqrt{(\delta\omega^2 + 2\omega_1^2)} \tag{22}$$

and

$$\tan \theta = \sqrt{2}\omega_1/\delta\omega. \tag{23}$$

To compare with the treatment here use is made of [23] to separate the multiplet spin $I_1=1/2$ for levels $M=1$ to 0. Hence the full equilibrium density matrix for $I=1$ is written

$$\begin{aligned} \sigma_1(0) &= 1/3 \left[E_1 + b\sqrt{3/2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right] \\ &= 1/3 \left[E_1 + b\sqrt{3/2} \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \right] + [\sigma_{1/2}(1)(t) - \frac{1}{2}E_{1/2}(1)], \tag{24} \end{aligned}$$

where [23]

$$\begin{aligned} \sigma_{1/2}(1)[0] &= \frac{1}{2}[E_{1/2}(1) + \phi_0^1(1)[0] \mathcal{Y}_{1/2}^{(1)0}(1)] \\ &= \frac{1}{2} \left| \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{array} \right) + b\sqrt{(1/6)} \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{array} \right) \right|, \end{aligned} \quad (25)$$

with $\phi_0^1(1)[0] = -ib/\sqrt{6}$. From (15), the effect of a selective pulse on $\mathcal{Y}_0^1(1)[0]$ leads to

$$\begin{aligned} &(\sigma_{1/2}(1)[(\alpha\beta)_{\phi_p}] - \frac{1}{2}E_{1/2}) \\ &= -i[\mathcal{D}_{10}^{(1)}(-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \mathcal{Y}_{1/2}^{(1)-1}(1) + \mathcal{D}_{00}^{(1)}(-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \\ &\quad \times \mathcal{Y}_{1/2}^{(1)0}(1) + \mathcal{D}_{-10}^{(1)}(-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \mathcal{Y}_{1/2}^{(1)-1}(1)] \frac{b}{\sqrt{6 \cdot 2}} \\ &= b/\sqrt{6} \begin{pmatrix} \frac{1}{2} \cos \beta & \frac{1}{2} \sin \beta \exp[-i(\phi_p - \alpha)] & 0 \\ \frac{1}{2} \sin \beta \exp[i(\phi_p - \alpha)] & \frac{1}{2} \cos \beta & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (26)$$

This recombines with (24) to give the same form as (19).

Note first that ω_{eff} and Ω_{eff} are the same and $\omega_{1,\text{eff}} = \sqrt{2}\omega_1$. Further define

$$\cos \theta = \frac{\delta\omega}{\Omega_{\text{eff}}}; \quad \sin \theta = \frac{\sqrt{2}\omega_1}{\Omega_{\text{eff}}} \quad (27)$$

which is consistent with $\tan \theta$ defined in [11], equation (28). Using these in equations (57-60) of [23] leads to

$$\cos \beta = \Lambda_1, \quad (28)$$

$$\exp[i(\alpha - \phi_p)] \sin \beta = \Lambda_2 \exp(-i\phi_p). \quad (29)$$

Actually [11] uses $\phi_p = 0$ (and $\omega_1 = -\omega_1$) so the agreement is complete.

The fact that the two results agree when applied to a single quantum selective excitation shows that the interaction term in the hamiltonian only lifts the degeneracy. The fact that the nuclear quadrupole interaction does not mix polarizations while the pulse is on is understandable in the treatment here, namely a multiplet spin 1/2 has no effective quadrupole term. For double and higher quantum excitation the quadrupole interaction can be effective as shown in § 8.

The results of this and the previous section are exact. For single quantum excitation (11) is not an approximation and the main result, (15), is obtained if both the r.f. field and the quadrupole interactions are included.

6. MULTIQUANTUM SELECTED EXCITATION BY PURE PULSES

Calculation of selective $|\Delta M| = |q| > 1$ transitions by selective irradiation introduces a complication which vanishes when $q = 1$. This is the possibility

of coupling between different multipoles of multiplet spin which is manifested in equation (12) by the sum over p'' . Examination of the terms in (12) reveals that the r.f. field leads to a 3- j coefficient

$$\begin{pmatrix} I & 1 & I \\ -M & q'' & M' \end{pmatrix}$$

indicating a multiquantum transition takes place in multiple jumps of $q'' = \pm 1$. This selection rule carries over to the multiplet spin. In particular the sum over all the multiplet spin polarizations, p'' , cannot lead to $|q''| > 1$ in (12). This suggests an approximation which removes the mathematical difficulties of summing over p'' , namely by choosing p'' equal to the tensor rank of the spin part of the hamiltonian, in this case $p'' = 1$. This approximation, called the multipole uncoupled model (MUM), ignores coupling between p and p' multipoles in (12) and forces $p = p'$. As a result of this approximation, multiquantum selective excitation can still be treated as pure rotation.

Putting $p'' = 1$ in (12) leads directly to the rotating frame multiplet spin equation,

$$\begin{aligned} \frac{\partial \hat{\phi}_q^p(I_M M)}{\partial t} = & \frac{i\omega_{1, \text{eff}}}{2} \exp [+i(\Delta\omega t - \phi_p)] \sqrt{[(p+q)(p-p+1)]} \hat{\phi}_{q-1}^p(I_M M) \\ & + \frac{i\omega_{1, \text{eff}}}{2} \exp [-i(\Delta\omega t - \phi_p)] \sqrt{[(p-q)(p+q+1)]} \\ & \times \hat{\phi}_{q+1}^p(I_M M), \end{aligned} \quad (30)$$

where the effective frequency corresponding to the multiplet spin I_M is

$$\begin{aligned} \omega_{1, \text{eff}} = & 3/2 \sum_{M_M = -I_M}^{I_M} \\ & \times \frac{\sqrt{[(I+M_1+M_M)(I-M_1-M_M+1)(I_M+M_M)(I_M-M_M+1)]}}{I_M(I_M+1)(2I_M+1)} \omega_1. \end{aligned} \quad (31)$$

For double quantum processes, $I_M = 1$ is required so each triplet of $M \leftrightarrow M-2$ has

$$\omega_{1, \text{eff}} = \frac{1}{2\sqrt{2}} [\sqrt{(I+M)(I-M+1)} + \sqrt{(I+M-1)(I-M+2)}] \omega_1. \quad (32)$$

For $I_M = 3/2$, triple quantum selective transition between levels $M \leftrightarrow M-3$ has

$$\begin{aligned} \omega_{1, \text{eff}} = & 1/10 [\sqrt{3} \sqrt{(I+M)(I-M+1)} + 2\sqrt{(I+M-1)(I-M+2)}] \\ & + \sqrt{3} \sqrt{(I+M-2)(I-M+3)}] \omega_1, \end{aligned} \quad (33)$$

etc.

The solution to equation (30) is again a pure rotation giving

$$\hat{\phi}_q^p(I_M M)[(\alpha\beta)_{\phi_p}] = \sum_{q'} \mathcal{D}_{qq'}^{(p)}(-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \hat{\phi}_q^p(I_M M)[0]. \quad (34)$$

It follows from (34) that excitation of a specific transition requires $\Delta\omega = \delta\omega \ll \omega_{1, \text{eff}}$ or from (18), (11) and (3) the applied r.f. field must obey

$$\omega \cong \omega_0 + \frac{3\tilde{Q}}{2I(2I-1)} (2M+q). \quad (35)$$

Note the off-resonance mismatch becomes easier to selectively satisfy with increasing \tilde{Q} , M or q , but harder to selectively satisfy with increasing total spin I .

In [23] an example of extracting a multiplet spin $I_{5/2}=3/2$ from a total spin $I=7/2$ was given (i.e. levels $5/2 \leftrightarrow -1/2$). The effect of a selective pulse on $\sigma_{3/2}(5/2)$ leads to (see equation (55) of [23])

$$\sigma_{3/2}(5/2)[(\alpha\beta)^{5/2-1/2}] = \frac{1}{4} \left[E_{3/2}(5/2) + \phi_0^1(5/2)[0] \sum_{q=-1}^1 \mathcal{D}_{q0}^{(1)} \right. \\ \left. \times (-(\phi_p - \alpha)\beta(\phi_p - \alpha)) \mathcal{Y}_{3/2}^{(1)q}(5/2) \right]. \quad (36)$$

From the representations of $\mathcal{Y}_{3/2}^{(1)q}(5/2)$, namely

$$\mathcal{Y}_{3/2}^{(1)0}(5/2) = \frac{i}{\sqrt{5}} \begin{pmatrix} 0 & . & . & . & . & . & . & 0 \\ 0 & \boxed{3} & 0 & 0 & 0 & . & . & . \\ 0 & 0 & 1 & 0 & 0 & . & . & . \\ 0 & 0 & 0 & -1 & 0 & . & . & . \\ 0 & 0 & 0 & 0 & -3 & . & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (37)$$

$$\mathcal{Y}_{3/2}^{(1)1}(5/2) = -i\sqrt{(6/5)} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \boxed{0} & 1 & 0 & 0 & . & . & . & . \\ 0 & 0 & 0 & 2/\sqrt{3} & 0 & . & . & . & . \\ 0 & 0 & 0 & 0 & 1 & . & . & . & . \\ 0 & 0 & 0 & 0 & 0 & . & . & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & . & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & . & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (38)$$

it is seen that this selective excitation on the *equilibrium* density matrix, although causing a triple quantum transition, i.e. population transfer between $M=5/2$ and $-1/2$, it (i) does not produce double or triple quantum coherence and (ii) it cannot invert the population between $M=5/2$ and $-1/2$. This underscores

a consequence of pure selective pulses, namely to produce double or triple quantum coherence, some $\phi^{(2)}$ or $\phi^{(3)}$ polarization must be present before the selective pulse is applied. Quadrupole coupling, if strong enough, changes this result as shown in the next two sections.

7. FINITE PULSES

In this section non-selective pulses are discussed. By finite we mean the pulses are applied for sufficiently long periods of time so that the quadrupole has time to couple while the pulse is on. This is of considerable importance for nuclei containing large quadrupoles giving a splitting about ω_0 which is too great for complete excitation by a single pulse. Often the pulse is applied off resonance at or near one or more of the quadrupole transition frequencies.

The approximation used here corresponds to the r.f. pulse being stronger than the quadrupole coupling, $|\omega_1| \gg |\omega_Q|$. The other limit $|\omega_Q| \gg |\omega_1|$ is not treated (see, however, the discussion). One reason for this lies in the evolution of the system under a strong \mathcal{H}_Q which tends to mix the multipoles together (see tables 1 and 3 of [20]) so that weak irradiation of one line mixes all the spectral lines making it difficult to be selective. In other words, what appears to be selective for single quantum lines may not be selective for higher multi-quantum processes.

To be specific weak pulses are usually called selective because by their nature they must be on for sufficient length of time to properly irradiate. This has the consequence that the envelope of excitation in the frequency domain is narrow, but internal interactions disperse the energy to other polarizations. In contrast if the pulse is applied for a short time and if the lines are sufficiently separated then the quadrupole has time to couple 'a little', so the limit $|\omega_1| > |\omega_Q|$ is appropriate. Such pulses distribute the order throughout the system to a lesser extent than 'long time' irradiation in the weak, $|\omega_1| < |\omega_Q|$, limit.

For the above reasons, the nomenclature 'finite pulse' is preferred over weak irradiation. Finite pulses fall into two main groups, namely weak finite pulses ($|\omega_1| < |\omega_Q|$) and strong finite pulses ($|\omega_1| > |\omega_Q|$).

Continuing the discussion of finite pulses, the effects of amplitude modulation in the ω_0 rotating frame can be expressed by using equations (13) and (42) of [20] to give (omitting the obvious terms)

$$\begin{aligned} \frac{\partial \hat{\phi}_q^k}{\partial t} = & 3/2q\tilde{Q}[\dots]^{1/2} \hat{\phi}_q^{k+1} - 3/2q\tilde{Q}[\dots]^{1/2} \hat{\phi}_q^{k-1} + i/2\omega_{+1} \exp(i\Delta\omega t - i\phi_p) \\ & \times \sqrt{(\dots)\hat{\phi}_{q-1}^k} + i/2\omega_{-1} \exp(-i\Delta\omega t + i\phi_p) \sqrt{(\dots)\hat{\phi}_{q+1}^k}, \quad (39) \end{aligned}$$

where the amplitude $\omega_1 = \gamma H_1$ is replaced with the time dependent amplitude modulated terms $\omega_{\pm 1}$ given by

$$\omega_{\pm 1}(t) = \gamma H_1 \exp(\mp i\omega_m t). \quad (40)$$

The treatment here of finite pulses can always account for simple amplitude modulation by modifying $\Delta\omega$ in (39) as a consequence of (40). The task remaining is to solve (39). The general solution can only reasonably be obtained numerically except for low I values. This is because the quadrupole interaction

mixes multipoles while simultaneously the r.f. field mixes orientations. For $I=1$, double quantum excitation and $I=3/2$, triple quantum excitations exact solutions are known [11]. These cases are particularly simple because the quadrupole cannot couple the highest multipole coherence ($\phi_{\pm 2}^2$ for $I=1$ and $\phi_{\pm 3}^3$ for $I=3/2$). The intermediate cases are complicated by multipole mixing. In the next section, the case of strong non-selective finite pulses is considered approximately followed by the treatments of selective finite pulses.

8. STRONG FINITE NON-SELECTIVE PULSES

In the limit that the adiabatic parameter $A \equiv |\Delta\omega/\omega_1|$ is large, the r.f. field has negligible effect on the polarizations. This case reduces to pure quadrupole evolution [20]. The other limit $A \cong 0$ corresponds to pure resonant pulses requiring all the spectral frequencies to be simultaneously excited by an r.f. pulse. In fact the experimental situation often encountered with spins with quadrupoles corresponds to $A < 1$ and, for a pulse of duration τ , $\omega_Q\tau \sim 1$ the quadrupole can couple while the pulse is on. This excitation, when non-selective, puts most of the intensity into the single quantum modes. However, such a pulse can be useful in producing non-zero multipole polarization $\phi_q^k \neq 0$ which can later be selectively separated.

Applying the transformation equation (43) of [20] to (39) diagonalizes the Zeeman part but causes the quadrupole part to be further mixed. Explicitly this is given by ($\omega_{\pm 1} = \omega_1$)

$$\begin{aligned} \frac{\partial \hat{\Psi}_{\bar{q}}^k}{\partial t} = & i\omega_1 q \hat{\Psi}_{\bar{q}}^k - \frac{i\hat{Q}}{(2I+1)} \left[\frac{(2I+3)(I+1)}{5I(2I-1)} \right]^{1/2} \left\{ \langle\langle \mathcal{Y}^{(k)} \| \mathcal{Y}^{(2)} \| \mathcal{Y}^{(k+1)} \rangle\rangle \right. \\ & \sum_{m'} (-1)^{k-\bar{q}} \begin{pmatrix} k & 2 & k+1 \\ -\bar{q} & m' & \bar{q} \end{pmatrix} d_{m'0}^{(2)}(\pi/2) \delta_{k',k+1} \\ & + \langle\langle \mathcal{Y}^{(k)} \| \mathcal{Y}^{(2)} \| \mathcal{Y}^{(k-1)} \rangle\rangle \sum_{m'} (-1)^{k-\bar{q}} \begin{pmatrix} k & 2 & k-1 \\ -\bar{q} & m' & \bar{q} \end{pmatrix} \\ & \left. \times d_{m'0}^{(2)}(\pi/2) \delta_{k',k-1} \right\} \hat{\Psi}_{\bar{q}}^{k'}, \quad (41) \end{aligned}$$

which is an exact result. The solution is obtained approximately using degenerate perturbation theory in the limit $|\omega_1| > |\hat{Q}|$. Inspection of (41) shows that all k have the same r.f. frequency when q is the same. This means that quadrupole terms $\hat{\Psi}_{\bar{q}}^{k+1}$ and $\hat{\Psi}_{\bar{q}}^{k-1}$ couple degenerately while $\bar{q} \neq \bar{q}$ couple non-degenerately. Therefore terms $\bar{q} \neq \bar{q}$ are dropped in the spirit of degenerate perturbation theory. If we go into the rotating frame of ω_1 ,

$$\hat{\Psi}_{\bar{q}}^k(t) \equiv \exp(-i\omega_1 t q) \hat{\Psi}_{\bar{q}}^k(t) \quad (42)$$

put $m' = 0$ (degenerate perturbation approximation), and use table 2 of [20], (41) reduces to

$$\frac{\partial \hat{\Psi}_{\bar{q}}^k}{\partial t} = -3/2 q \hat{Q}_{\text{eff}}[\dots]^{1/2} \hat{\Psi}_{\bar{q}}^{k+1} + 3/2 q \hat{Q}_{\text{eff}}[\dots]^{1/2} \hat{\Psi}_{\bar{q}}^{k-1}. \quad (43)$$

Equation (43) is identical to (13) of [20] except that the quadrupole strength is reduced to $\tilde{Q}_{\text{eff}} = -\tilde{Q}/2$ due to the term, $d_{00}^{(2)}(\pi/2) = -1/2$ (in 41). Hence all the solutions in tables 1 and 3 of [20] are valid for $\Psi_{\bar{q}}^{k}$ when \tilde{Q} is replaced by \tilde{Q}_{eff} .

In order to retrieve the $\hat{\phi}_q^{k_s}$, the general form of the solution from [20] (table 3) is written

$$\hat{\Psi}_{\bar{q}}^{k}(t) = \sum_{k'} M_{\bar{q}}^{kk'}(t) \hat{\Psi}_{\bar{q}}^{k'}(0). \tag{44}$$

Transforming back the $\hat{\phi}_q^k$ gives

$$\hat{\phi}_q^k(t) = \sum_{k' \bar{q} \bar{q}'} \mathcal{D}_{\bar{q}\bar{q}'}^{(k)}(\Delta\omega - \phi_p, \pi/2, 0) \exp(i\omega_1 \bar{q}t) M_{\bar{q}}^{kk'}(t) \mathcal{D}_{\bar{q}\bar{q}'}^{(k')} \times (0, \pi/2, \phi_p) \hat{\phi}_q^{k'}(0). \tag{45}$$

Consider $k=1, q=1$, for $I=3/2$. From table 3 [20] the coefficients are

$$\left. \begin{aligned} M_0^{11}(t) &= 1, \\ M_{\pm 1}^{11}(t) &= 1/5(2 + 3 \cos \tilde{Q}_{\text{eff}}t), \\ M_{\pm 1}^{12}(t) &= \pm \sqrt{3/5} \sin \tilde{Q}_{\text{eff}}t, \\ M_{\pm 1}^{13}(t) &= \sqrt{6/5}(1 - \cos \tilde{Q}_{\text{eff}}t). \end{aligned} \right\} \tag{46}$$

In the limit $\tilde{Q}_{\text{eff}}t \rightarrow 0$, i.e. short pulses, the only non-zero terms are $M_0^{11}(t) = M_1^{11}(t) = 1$ and the pure pulse result of a rotation is obtained from (45). Since this is a perturbation treatment in the limit $|\omega_1| > |\omega_Q|$, the opposite limit $|\omega_1| \ll |\omega_Q|$ is not applicable.

Equation (45) has a physically revealing structure. In essence both r.f. evolution (via $\exp(i\omega_1 \bar{q}t)$) and quadrupole evolution (via $M_{\bar{q}}^{kk'}(t)$) are occurring simultaneously while the \mathcal{D} s rotate $\hat{\phi}_q^k$ and $\hat{\phi}_q^{k'}$ to a common axis. By combining both pulse and quadrupole terms, all the multipoles can be excited as well as various multiquantum coherences.

From equation (45), by including quadrupole interactions, the creation of multiquantum coherence by irradiating at equilibrium is possible. For example for $I=3/2$, a pulse produces triple quantum coherence according to

$$\hat{\phi}_{\pm 3}^3(t) = \exp[\pm i3(\Delta\omega t - \phi_p)] \frac{i}{4} \sqrt{\left(\frac{3}{10}\right)} \sin(\omega_1 t) (1 - \cos \tilde{Q}_{\text{eff}}t) \hat{\phi}_0^1(0). \tag{47}$$

9. FINITE SELECTIVE PULSES

The treatment of selective finite pulses follows exactly the same procedure as for pure selective pulses, § 3. The general equation for the multiplet spin polarizations, (7) is the starting point into which the full r.f. plus quadrupole hamiltonian is substituted. In this section the case of strong finite pulses is treated, namely $|\omega_1| > |\omega_Q|$.

One difficulty with finite pulses lies in the fact that the quadrupole hamiltonian acts on the whole system while the r.f. part acts only on a part. This problem is trivially avoided when the initial density matrix is diagonal ($q=0$) or only the highest multipole ($\phi_{\pm 2I}^{2I}(0)$) is excited since both are constants of the motion in the rotating frame. Otherwise, it is necessary to separate the density operator into two parts, namely the multiplet spin part $\sigma_{I_M}(M)$ (evolving under the r.f. and quadrupole interaction) and the remainder, $\sigma_I(R)$, which evolves only under the quadrupole. Therefore the initial density operator is expressed as

$$\sigma_I[0] = \sigma_{I_M}(M)[0] + \sigma_I(R)[0]. \quad (48)$$

Each can be treated separately and then recombined as was done in § 5.

The multipole uncoupled model is used and requires $p''=1$ for the r.f. part and $p''=2$ for the quadrupole part. The resulting equation is identical to (39) except that $\omega_{\pm 1}$ is replaced by $\omega_{1, \text{eff}}$ (see (31)) and \tilde{Q} is replaced by \tilde{Q}_{eff} given by

$$\tilde{Q}_{\text{eff}} = \frac{5\tilde{Q}}{I(2I-1)(2I_M+1)(2I_M+3)} \sum_{M_M=-I_M}^{I_M} (3M_M^2 - I_M(I_M+1)) \times (3(M_1 + M_M)^2 - I(I+1)). \quad (49)$$

One immediate conclusion is that the effective quadrupole is zero for single quantum selective excitation. Hence, the multiplet spin operator $\sigma_{1/2}(M)$ responds as shown in §§ 4 and 5 even for finite pulses.

For double quantum processes the effective quadrupole is the same for all triplets, namely

$$\tilde{Q}_{\text{eff}} = \frac{2\tilde{Q}}{I(2I-1)}, \quad (I_M=1). \quad (50)$$

For triple quantum processes, all multiplet spins have effective quadrupoles of

$$\tilde{Q}_{\text{eff}} = \frac{75}{16I(2I-1)} \tilde{Q}, \quad (I_M=3/2). \quad (51)$$

In both cases $\tilde{Q}_{\text{eff}} < \tilde{Q}$ since, for $I_M=1$, $I > 1$ and for $I_M=3/2$, $I > 3/2$. As I increases, the effective quadrupole becomes smaller.

A decreasing effective quadrupole strength (see (49)) and an increasing effective r.f. strength (see (31)) combine to favour a treatment where the pulses are either pure or are treated as a perturbation in the limit $|\omega_{1, \text{eff}}| > |\tilde{Q}_{\text{eff}}|$ for selective excitation.

The actual solutions using \tilde{Q}_{eff} are not given since the perturbation results in the strong limit are found from the treatment in § 8. The set of equations for the multiplet spin polarization $\hat{\phi}_q^p(I_M M)$ are given by (39) (with $k \rightarrow p$, $\omega_{\pm 1} \rightarrow \omega_{1, \text{eff}}$, $\tilde{Q} \rightarrow \tilde{Q}_{\text{eff}}$), and lead directly to (43) with solutions given by (45).

This section shows that a given multiplet spin, taken from the full spin manifold, can be treated in the same way that non-selective finite pulses are treated. The modifications lie in replacing both ω_1 and \tilde{Q} by their effective values.

10. SUMMARY

The main results of this paper for pulses on single spins of any magnitude are summarized.

- (i) Pure (δ -function) selective pulses can be treated exactly for multiplet spin $1/2$ and approximately with the help of MUM multiplet spin $I_M > 1/2$. The solution is a pure rotation confined to the multiplet of $2I_M + 1$ M levels within the full spin manifold. In all selective excitation, an effective r.f. amplitude, $\omega_{1, \text{eff}}$, arises which is greater than ω_1 . For single quantum selective excitation the results agree completely with the fictitious spin result.
- (ii) Strong finite non-selective pulses can involve the full density matrix which can be solved using degenerate perturbation theory in the limit $|\omega_1| > |\omega_Q|$. The quadrupole can then couple, but not dominate, while the pulse is being applied. The resulting set of equations have been solved for $I \leq 9/2$ [20].
- (iii) For strong finite selective pulses, the solutions are found to be identical to that for non-selective pulses but restricted to the multiplet spin density operator. Both the r.f. amplitude ω_1 and quadrupole strength, \tilde{Q} are replaced by effective values. In all cases it is found that $|\omega_{1, \text{eff}}| > |\omega_1|$ and $|\tilde{Q}_{\text{eff}}| < |\tilde{Q}|$, thereby making the pulse effectively stronger and purer.

The results of this paper should be applicable to systems containing uncoupled or weakly coupled spins of magnitude I . The clearest physical picture emerges when the multiplet spin polarizations are simply rotated by pure selective pulses. When a distribution of quadrupole strengths occurs, or when the quadrupole is too large for pure pulses to excite all the lines, the situation reduces to strong finite pulses. The perturbation treatment of § 8 is obtained with these cases in mind.

11. DISCUSSION

The results obtained for single quantum selective excitation are exact. For the higher selective multiquantum excitation the multipole uncoupled model is proposed. This approximation ignores coupling between multipoles except for those allowed by the full hamiltonian. Therefore equation (7) restricts p'' to the tensor rank of the spin part of the hamiltonian, namely $p'' = 1$ for an r.f. (Zeeman) interaction and $p'' = 2$ for a nuclear quadrupole interaction.

It is appropriate to make some remarks regarding weak finite pulses (long time irradiation with $|\omega_1| < |\omega_Q|$ and $|\omega_Q t| \gg 1$). This case can also be treated by perturbation theory. Starting from equation (39) (with $\omega_{\pm 1} = \omega_1$), the set of equations can be cast into a form which diagonalizes the quadrupole part. The pure quadrupole case has been solved previously [20] and the matrices \mathcal{T} which diagonalize the quadrupole part are known. Applying this transformation to (39) gives

$$\frac{\delta \hat{\chi}_q^k}{\delta t} = i\omega_q^{\bar{k}} \chi_q^{\bar{k}} + i\omega_1 \sum_{\bar{k}'\bar{q}} Z_{q\bar{q}'}^{\bar{k}\bar{k}'} \hat{\chi}_{q'}^{\bar{k}'}, \quad (52)$$

where

$$\hat{\chi}_q^{\bar{k}} \equiv \sum_k (\mathcal{T}^{-1})_q^{\bar{k}k} \hat{\phi}_q^k \quad (53)$$

and

$$\begin{aligned} Z_{qq'}^{\bar{k}\bar{k}'} &= \sum_k (\mathcal{T}^{-1})_q^{\bar{k}k} [\sqrt{[(k+q)(k-q+1)]} \delta_{q',q-1} \\ &\quad + \sqrt{[(k-q)(k+q+1)]} \delta_{q',q+1}] (\mathcal{T})_{q'}^{k\bar{k}'} \\ &\quad \times \exp [i(\Delta\omega t - \phi_p)(q-q')]. \quad (54) \end{aligned}$$

The quadrupole multiquantum frequencies $\omega_q^{\bar{k}}$ are also given in [20].

Since $q \neq q'$, there is no degenerate coupling as in the strong finite pulse case, § 7, except for accidental degeneracies between different multiquantum coherences. However from table 1 of [20] there are numerous degeneracies arising for all multiquantum processes for half integer spins but no degenerate coupling for integer spins. The latter case gives, for $|\omega_1| \ll |\omega_q^k|$, no first order coupling and a second order coupling of

$$\omega_q^{\bar{k}} \rightarrow \omega_q^{\bar{k}} - \omega_1^2 \sum_{\bar{k}'q'} \frac{|Z_{qq'}^{\bar{k}\bar{k}'}|^2}{\omega_q^{\bar{k}} - \omega_{q'}^{\bar{k}'}} \quad (55)$$

giving a correction of $|\omega_1^2/\tilde{Q}|$ in agreement with [11–12]. For degenerate cases, the leading perturbation terms usually give 2×2 submatrices for the frequency pairs $\omega_q^{\bar{k}} = \omega_{q'}^{\bar{k}'}$ with perturbed frequencies of

$$\omega_q^{\bar{k}} \rightarrow \omega_q^{\bar{k}} \pm \sqrt{[(\omega_q^{\bar{k}})^2 + |Z_{qq'}^{\bar{k}\bar{k}'}|^2 \cdot \omega_1^2]}, \quad (56)$$

again in agreement with [11] for the special cases of $I=3/2$. For higher half integral spins ($I \geq 7/2$), 3×3 degenerate submatrices occur.

The question arises as to the feasibility of analysing weak irradiation. First it is remarked that in spite of the narrow frequency range being irradiated, to which the terminology 'selective' is applied, in fact strong internal couplings disperse the energy to many other modes thereby obviating selectivity. Although weak irradiation is easy to do experimentally, it is the most difficult type of pulse to analyse mathematically. In contrast, short finite pulses, if possible to create, permit straightforward calculations to be done which reveal how all the polarizations are evolving.

In a recent paper by Hatanaka [13] it is shown how strong non-selective pulses $((\pi/4)_0 - \tau_1 - (\pi/2)_{\phi_2} - \tau_2)$ can produce coherence transfer in a spin 1 system. This has been analysed in terms of multipoles [26]. It provides an example of selective excitation by non-selective irradiation.

In some cases, however, it is impossible to do better than weakly irradiate. When this is the case it is noted that for single spins of any magnitude of interest, the spin dynamics can be calculated numerically from any initial state using equation (39). Such treatments would permit quantitative analysis in both strong and weak finite pulse limits to be performed in conjunction with the experimental program.

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