Magnetic multipoles in time dependent fields

B. C. Sanctuary

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada H3A 2K6

(Received 22 May 1979; accepted 1 October 1979)

The effects of time dependent magnetic vector fields on magnetic multipoles is presented. It is shown that a single rapid pulse causes the q^{th} spherical component of the k^{th} multipole in the rotating frame to evolve as the associated Legendre function $P_k^q(\cos\theta)$ at resonance. The initial state for multispin systems which is prepared by such a pulse is given.

I. INTRODUCTION

The use of a pulse of oscillating radio frequency radiation to turn magnetic vectors is commonplace and technologically highly advanced.[1] By definition, a rapid pulse is a time dependent magnetic field applied for a duration such that relaxation processes and internal couplings are not appreciable. Further, the pulse is usually applied "at resonance," defined as the Larmor precession frequency of the spin, ω_0, in a static magnetic field. The part of the magnetic field which excites a spin can be considered to be a Fourier component of a pulse of short duration which has a correspondingly large frequency spread. If the amplitude of the oscillatory field is small with respect to the static field, then off-resonance pulses lead to negligible effect on the magnetization.

These effects are well known for the magnetic vector polarizations, but the results for higher multipoles and cross polarizations are not known. Knowledge of these is important for three reasons.

(1) Spins with $I \geq 1/2$ have quadrupoles and higher multipoles up to $k = 2I$.

(2) Multispin systems can be prepared in an initial state either selectively or nonselectively by pulse synthesization from desired frequency components.

(3) Spin density operators for multispin systems contain multipoles higher than a vector as well as cross polarization tensors.

Each of these three points requires knowledge of the effects of the state preparing pulse on the multipoles for a proper description of the initial state selection in magnetic resonance experiments. The purpose of this paper is to study the effects of such a pulse on multispin systems containing spins of arbitrary magnitude I_i. The main result is that under the usual conditions of an experimental pulse, a spin $I_i > 1/2$ initially at equilibrium in a static magnetic field (H_0) and which turns the vector polarization by $\cos\omega_1\tau$ (where $\omega_1 = +\gamma H_1$) also turns the quadrupole polarization by $P_2(\cos\omega_1\tau)$, the octapole by $P_3(\cos\omega_1\tau)$, and so on, up to tensor rank $k = 2I$. $P_k(\cos\omega_1\tau)$ are the Legendre polynomials, and τ is the duration of the pulse.

The treatment here starts with the equation describing the time evolution of the kth multipole polarization tensor in the presence of a time-dependent vector magnetic field[2] $\mathbf{H}(t)$. For short times when the different spin species do not have time to couple and when relaxation effects are negligible, the Hamiltonian is taken as

$$\mathcal{H} = -\hbar \sum_{i=1}^{n} \gamma_i \mathbf{I}_i \cdot \mathbf{H}(t) \ . \tag{1}$$

Under these conditions the various magnetic multipoles of tensor rank $k \leq 2I$ uncouple from each other. This means that for each multipole of tensor rank k there are a maximum number of only $2k+1$ coupled equations to be solved. Moreover, it has been shown that only oscillatory solutions occur for these $2k+1$ components and the magnitude of the initial polarization is conserved for the duration of the pulse for any time dependent field.[2]

In Ref. 2, two types of magnetic fields are distingushed, namely, resonant and nonresonant. The nonresonant fields lead to feedback effects which are difficult to control while, as is shown here, a resonant field with an oscillatory exponential time dependence can be solved exactly, even off resonance. However, at resonance, the well-known result for vector magnetization, namely, that the effective field is a constant in the rotating frame, is shown to be valid for all the multipoles. Moreover, the resonance condition is always $\omega = \omega_0$, even for the $q\omega_0$ harmonics, $-k \leq q \leq k$, for each kth multipole.

In Sec. II the equation governing the time dependence of the kth multipole for a single spin under the influence of the Hamiltonian (1) is reviewed, and the general resonance solutions are presented.

The nonresonance case is not easily treated in general because the algebra involved becomes excessive. However, in Sec. III the result for the $q = 0$ spherical component of the quadrupole is given, while the Appendix presents a summary of the approach.

Finally, the case of multispin systems is treated in Sec. IV.

II. TIME DEPENDENCE OF MULTIPOLES FOR A SINGLE SPIN IN AN OSCILLATING MAGNETIC FIELD

The procedure here makes use of the spin density operator formulation for a single spin of fixed magnitude I. The density operator is expanded in a multipole series[2,3] in terms of normalized symmetric traceless tensors of rank k, $\mathcal{Y}^{(k)}(\mathbf{I})$,

$$\sigma = \frac{1}{2I+1} \sum_{k=1}^{2I} \mathcal{Y}^{(k)}(\mathbf{I}) \odot^k \phi^{(k)} \ , \tag{2}$$

where $\phi^{(k)}$ is the k multipole for the ith spin. A spherical basis $e^{(k)q}$ is defined such that the complex conjugate

 0021-9606/80/151048-06$01.00

obeys

$$e^{(k)q^*} = (-1)^q e^{(k)-q} \equiv e_q^{(k)} \tag{3}$$

and

$$e^{(k)q} \odot^k e_{q'}^{(k)} = \delta_{qq'} \ , \tag{4}$$

where $\odot^k$ denotes the k-fold dot product of nearest indices. It then follows that the spherical components of $\phi^{(k)}$, namely

$$\phi^{(k)q} = \phi^{(k)} \odot^k e^{(k)q} = \phi_q^{(k)^*} \ , \tag{5}$$

are related to the matrix elements of σ,

$$\sigma^I_{MM'} \equiv \langle IM | \sigma | IM' \rangle \ , \tag{6}$$

by [see Ref. 4, Eq. (29)]

$$\phi^{(k)q} = \sum_{MM'=-I}^{I} (2I+1)^{1/2} \times (-1)^{I-M'} (2k+1)^{1/2} \begin{pmatrix} I & k & I \\ -M & -q & M' \end{pmatrix} \sigma^I_{MM'} \ . \tag{7}$$

In particular, it is assumed that the initial polarizations are aligned in the z direction defined by a static magnetic field. Hence the populations of the IM levels, $p_M \equiv \sigma^I_{MM}$, are chosen to obey

$$\sum_{M=-I}^{I} p_M = 1 \ . \tag{8}$$

The various z components of the multipoles are related to the populations by

$$\phi^{(1)0} = \sqrt{\frac{3}{I(I+1)}} \sum_{M=-I}^{I} M p_M \ , \tag{9}$$

$$\phi^{(2)0} = \sqrt{\frac{5}{I(I+1)(2I-1)(2I+3)}} \sum_{M=-I}^{I} [3M^2 - I(I+1)] p_M \ , \tag{10}$$

and in general

$$\phi^{(k)0} = (2I+1)^{1/2} (2k+1)^{1/2} \sum_{M=-I}^{I} \begin{pmatrix} I & I & k \\ M & -M & 0 \end{pmatrix} p_M \ . \tag{11}$$

One choice of initial polarization used here is to take $p_I = 1$ and $p_{M \neq I} = 0$. After a pulse the populations are redistributed into the other $2k$ components of the *same* multipole.

In the presence of a time-dependent magnetic field and a Hamiltonian of the form of Eq. (1), the multipoles satisfy[2]

$$d\phi_q^{(k)}/dt = -i\gamma [k(k+1)(2k+1)]^{1/2} \times \sum_{mq'} (-1)^{k-q} \begin{pmatrix} 1 & k & k \\ m & -q & q' \end{pmatrix} H_m(t) \phi^k_{q'} \ , \tag{12}$$

where

$$H_0(t) = H_z(t), \quad \text{and} \quad H_\pm(t) = \mp \frac{1}{\sqrt{2}} [H_x(t) \mp i H_y(t)] \ . \tag{13}$$

In particular, it is seen that the multipoles of different tensor rank uncouple, while the $2k+1$ components form a coupled set of first order differential equations for which, as stated above, only oscillatory solutions exist.[2] It is also evident that each equation is independent of the spin I. Therefore, *except* for γ the same multipoles of different spins have the same time dependence in a magnetic field.

The particular form for the magnetic field used in pulsed NMR spectrometers is a constant static z field $H_0(t) = H_0$ and a field of amplitude $H_1 \ll H_0$ applied for a time τ in the x, y plane. Such a pulse can be synthesized to contain only the frequency components needed for a selective excitation. Mathematically this is equivalent to taking only the desired components from the Fourier series and mixing them. One such component is

$$H(t) = \hat{x}\tilde{H}_1(\omega) \cos\omega t - \hat{y}\tilde{H}_1(\omega) \sin\omega t + H_0 \hat{z} \tag{14}$$

$$= \sum_{m=-1}^{1} e^{(1)m} H_m(t) \ , \tag{15}$$

where

$$H_m(t) = \left(\delta_{m0} H_0 - m \frac{\tilde{H}_1(\omega)}{\sqrt{2}} e^{im\omega t} \right) \tag{16}$$

and

$$\tilde{H}_1(\omega) = H_1 \frac{\sin\omega\tau}{\omega\tau} \ . \tag{17}$$

By defining the rotating frame as

$$\hat{\phi}_q^{(k)} = e^{-iq\omega_0 t} \phi_q^{(k)} \tag{18}$$

and the frequencies

$$\omega_1 = \gamma \tilde{H}_1(\omega) \ , \quad \text{and} \quad \omega_0 = \gamma H_0 \ , \tag{19}$$

Eq. (12) becomes

$$\frac{d\hat{\phi}_q^{(k)}}{dt} = i\omega_1 \frac{[k(k+1)(2k+1)]^{1/2}}{\sqrt{2}} \times \sum_{mq'} (-1)^{k-q} \begin{pmatrix} 1 & k & k \\ m & -q & q' \end{pmatrix} m \, e^{-i(q-q')\omega_0 t} e^{im\omega t} \hat{\phi}_{q'}^{(k)} \ . \tag{20}$$

At resonance, $\omega = \omega_0$. This condition, along with conservation of angular momentum $m = q - q'$ results in the time dependence of the exponential vanishing, rendering the effective magnetic field a constant. However, each multipole obeys the following set of equations both on and off resonance.:

$$\frac{d\hat{\phi}_q^{(k)}}{dt} = \frac{i\omega_1}{2} \Big[\sqrt{(k-q)(k+q+1)} \exp[+i(\omega_0 - \omega)t] \hat{\phi}_{q+1}^{(k)} + \sqrt{(k+q)(k-q+1)} \exp[-i(\omega_0 - \omega)t] \hat{\phi}_{q-1}^{(k)} \Big] \ . \tag{21}$$

In both the on and off resonance cases it is straightforward, although tedious for nonresonant large k, to obtain analytical solutions. Each spherical component q is coupled to the components $q \pm 1$ except for $q = \pm k$, whence

$$\frac{d\hat{\phi}^k_{\pm k}}{dt} = i\omega_1 \sqrt{\frac{k}{2}} \exp[\mp i(\omega_0 - \omega)t] \hat{\phi}^k_{\pm(k-1)} \ . \tag{22}$$

The simplicity of these equations follows from the fact that the interaction, Eq. (1), involves only vector spin operators which, in the spherical basis used here, are decomposed into raising and lowering operators. The z component is removed by the rotating frame transformation, Eq. (18).

If a magnetic interaction of tensor character were used instead of Eq. (1), or relaxation and/or spin coupling effects played a role, much of the simplicity of a vector magnetic field would be lost. This is due to the fact that fields of quadrupole or higher tensor rank lead to coupling between different multipoles, as does the presence of internal couplings to other spins or local fields produced by fluctuating internal motions.

The resonance solution to Eq. (21) is easily obtained. By setting $\omega=\omega_0$, changing variables from t to $z=\cos\omega_1 t$, and making the substitution

$$\hat{\phi}^k_q=(-i)^q\sqrt{\frac{(k-q)!}{(k+q)!}}\,f^q_k \ , \tag{23}$$

it is found that

$$2(1-z^2)^{1/2}\frac{df^q_k}{dz}=-f^{q+1}_k+(k+q)(k-q+1)\,f^{q-1}_k \ . \tag{24}$$

This is a recursion relation for the associated Legendre functions,[5] hence $f^k_q=P^k_q(\cos\omega_1 t)$, or for a pulse of duration τ,

$$\hat{\phi}^k_q(\tau)=(-i)^q\sqrt{\frac{(k-q)!}{(k+q)!}}\,P^q_k(\cos\omega_1\tau) \ . \tag{25}$$

In the laboratory frame, the functions are related to the spherical harmonics by

$$\phi^{(k)}_q(\tau)=\sqrt{\frac{4\pi}{2k+1}}\,(-i)^q\,Y_{kq}(\omega_1\tau,\ \omega_0\tau) \ . \tag{26}$$

These resonance solutions show that the kth multipole components all oscillate, except for normalization, as the associated Legendre functions in the rotating frame and as spherical harmonics in the laboratory frame.

In this section, the initial $\hat{z}$ polarizations have been chosen as unity, in order to keep the normalization simple. In practice, one may choose, for example, $p_I=1$, $P_{M\neq I}=0$ as the initial population distribution in a static z field before the pulse. Then the initial polarizations are given by Eqs. (9) and (11). The effect of the resonance field on the $q=0$ component is then seen to have a classical analogue by identifying

$$\cos\omega_1\tau=M/\sqrt{I(I+1)} \tag{27}$$

in Eqs. (9)–(11).

The effect of various pulses can be envisaged. For example, a $\pi/2$ pulse which destroys the z components of the magnetic dipole also destroys the $q=0$ components of all the odd multipoles and at the same time reverses the quadrupole polarization.

III. NONRESONANCE SOLUTIONS

When $\omega\neq\omega_0$, a general solution was not found, although with enough effort, analytical solutions can always be obtained. The difficulty lies in that the transformation matrix, see Eq. (21), becomes time dependent off resonance. This time dependence causes additional mixing between the components of a given multipole. A transparent way of viewing this is to introduce the transformation

$$\tilde{\phi}^{(k)}_q(t)=e^{i\Delta q t}\,\hat{\phi}^{(k)}_q(t) \ , \tag{28}$$

where

$$\Delta=(\omega_0-\omega) \ . \tag{29}$$

Equation (21) then becomes

$$\frac{d\tilde{\phi}^{(k)}_q(t)}{dt}=\frac{i\omega_1}{2}\left[\sqrt{(k-q)(k+q+1)}\ \tilde{\phi}^{(k)}_{q+1}+\sqrt{(k+q)(k-q+1)}\ \tilde{\phi}^{(k)}_{q-1}\right]+iq\Delta\,\tilde{\phi}^{(k)}_q(t) \ . \tag{30}$$

Hence the nonresonance set of equations formally differs from the resonance set [Eq. (21) with $\omega=\omega_0$ or Eq. (24)] by the presence of a nonhomogeneous term which is proportional to Δ.

Off-resonance solutions are now obtained to illustrate the physical meaning. In general, the solutions for particular k can be found by the Laplace transform method. Alternatively, one can generate a differential equation along with initial conditions for $\phi^{(k)}_0(t)$ or calculate the state using rotation matrices. The amount of algebra in both approaches is about the same.

The differential equations for $\phi^k_0(t)$ are homogeneous at order $2k+1$. The coefficients are constant. Hence the solutions are a sum of $2k+1$ exponentials with the characteristic polynomials given by

$$\tilde{\phi}^{(k)}_0(\tilde{\phi}^{(k)}_0-i\Omega)(\tilde{\phi}^k_0+i\Omega)(\tilde{\phi}^{(k)}_0-i2\Omega)\times(\tilde{\phi}^{(k)}_0+i2\Omega)\cdots(\tilde{\phi}^{(k)}_0-k\Omega)(\tilde{\phi}^{(k)}_0+ik\Omega)=0 \ , \tag{31}$$

where $\Omega=\sqrt{\omega_1^2+\Delta^2}$. The solutions all take the form

$$\tilde{\phi}^{(k)}_0(\tau)=\sum_{l=-k}^{k}C^{(k)}_l\,e^{il\Omega\tau} \ , \tag{32}$$

where the constant coefficients $C^{(k)}_l$ are determined by the initial conditions

$$\phi^{(k)}_q(0)=\delta_{q,0} \tag{33}$$

and obey

$$\sum_{l=-k}^{k}C^{(k)}_l=1 \ . \tag{34}$$

Moreover, it can be shown that all the odd derivatives of $\tilde{\phi}^{(k)}_0(\tau)$ must vanish, thereby establishing that

$$C^{(k)}_l=C^{(k)}_{-l} \ . \tag{35}$$

On the other hand, no simple method was found for obtaining the even derivatives, and the algebra involved increases rapidly with k. The second and fourth initial derivatives are

$$\ddot{\tilde{\phi}}^{(k)}_0(0)=-\omega_1^2\,\frac{k(k+1)}{2} \tag{36}$$

and

$$\ddot{\ddot{\tilde{\phi}}}{}^{(k)}_0(0)=\{\omega_1^2\tfrac{1}{2}[k(k+1)+\tfrac{1}{2}(k-1)(k+2)]+\Delta^2\}\left(\omega_1^2\,\frac{k(k+1)}{2}\right) \tag{37}$$

using Eq. (33).

For the magnetic dipole, $k=1$, the solutions are given in Ref. 2.

For a magnetic quadrupole, $k=2$, the solution is

$$\tilde{\phi}^{(2)}_0(\tau)=C^{(2)}_0+2C^{(2)}_1\cos\Omega\tau+2C^{(2)}_2\cos2\Omega\tau \ , \tag{38}$$

where

$$C_0^{(2)} = \frac{1}{\Omega^4}(\Delta^4 - \Delta^2\omega_1^2 + \tfrac{1}{4}\omega_1^4) \ , \tag{39}$$

$$C_1^{(2)} = \tfrac{3}{2}(\omega_1^2\Delta^2/\Omega^4) \ , \tag{40}$$

and

$$C_2^{(2)} = \tfrac{3}{8}(\omega_1^4/\Omega^4) \ . \tag{41}$$

At resonance, $\omega = \omega_0$ and

$$C_0^{(2)} = \tfrac{1}{4} \ , \quad C_1^{(2)} = 0 \ , \quad \text{and} \quad C_2^{(3)} = \tfrac{3}{8} \ , \tag{42}$$

in which case $\tilde{\phi}_0^{(2)}$ becomes $P_2(\cos\omega_1\tau)$, in agreement with the previous section.

In the Appendix the equations of this section are derived in more detail.

For an NMR pulse, the physical consequence of the off-resonance solutions can be seen. If the rf amplitude ω_1 is small with respect to $|\omega - \omega_0|$, $\phi_0^{(2)}(\tau)$ is a constant. This can be viewed in terms of a parameter α, defined by

$$\alpha = \left|\frac{\omega - \omega_0}{\omega_1}\right| \ . \tag{43}$$

In terms of α, Eqs. (39)–(41) become

$$C_0^{(2)} = \frac{1}{(1+\alpha^2)^2}(\alpha^4 - \alpha^2 + \tfrac{1}{4}) \to 1 \quad \text{for} \quad \alpha \gg 1 \ , \tag{44}$$

$$C_1^{(2)} = \frac{3}{2}\frac{\alpha^2}{(1+\alpha^2)^2} \to 0 \quad \text{for} \quad \alpha \gg 1 \ , \tag{45}$$

$$C_2^{(2)} = \frac{3}{8}\frac{1}{(1+\alpha^2)^2} \to 0 \quad \text{for} \quad \alpha \gg 1 \ , \tag{46}$$

along with their large α limits. Clearly, for $\alpha \gg 1$, $\hat{\phi}^{(2)0}(\tau) = 1$. That is, for small rf amplitude and nonresonance conditions, the polarization is time independent and the initial polarization retains its value for all time. If as is often the case, $|\omega_1|$ is very small with respect to $|\omega_0|$, then α is only small (or zero) near (at) resonance. The same situation exists for off-resonance solutions for $\phi^{(1)0}(\tau)$. It is expected that the higher multipoles behave similarly.

The consequence of this for pulsed NMR techniques is simply that for small amplitude pulses, the multipole polarizations are significantly affected only at resonance.

For a discussion of α in terms of adiabaticity, see Refs. 2 and 6.

IV. RESONANCE PULSE ON MULTISPIN SYSTEMS

In practical situations, a system containing several spins is subjected to a pulse, or a series of pulses, in order to prepare the state. Although pulses are used for a variety of purposes, including decoupling of spins, the main object of this section is to give the expressions for the nonequilibrium state of a spin system after a pulse on a system initially at equilibrium in a large static magnetic field. Such a prepared nonequilibrium state is used experimentally to measure relaxation rates. The results of this section thus give the initial conditions needed for the solution of relaxation equations for multispin systems which govern the relaxation phenomena.

As the number of spins increases, the number of operators required to span the spin space rapidly increases. One operator basis is just the product space,

$$|I_1 M_1 I_2 M_2 \cdots I_n M_n\rangle\langle I_1 M_1' I_2 M_2' \cdots I_n M_n'| \ . \tag{47}$$

On the other hand, it is possible to construct a set of irreducible tensor operators which do the same job,[4] namely, $T_{\{K\}}^{(k)q}(k_1 k_2 \cdots k_n)^z$. Here k_i corresponds to the tensor rank of the ith spin with the limits $0 \le k_i \le 2I_i$. The set $\{K\}$ corresponds to $n-2$ intermediate values which differ with the coupling scheme used (denoted by z), while k and q are the overall rank and spherical component of the tensor. In terms of the $\mathcal{Y}$'s in Eq. (2), the T's are (see Ref. 7 or 4)

$$T_{\{K\}}^{(k)q}(k_1 k_2 \cdots k_n)^z \equiv \left[\prod_{i=1}^{n}(2I_i+1)^{-1/2}\right] \times \sum_{\substack{q_i \\ i=1,n}} \langle k_1 q_1 k_2 q_2 \cdots k_n q_n | (k_1 k_2 \cdots k_n)^z \{K\} kq\rangle \times \mathcal{Y}^{(k_1)q_1}(I_1)\mathcal{Y}^{(k_2)q_2}(I_2)\cdots\mathcal{Y}^{(k_n)q_n}(I_n) \ . \tag{48}$$

The important point concerning the T's is that they can be used as a basis to completely span the spin space. Hence the density operator becomes

$$\sigma = \sum_{kq}\sum_{\substack{k_i \\ i=1,n}}^{2I_i}\sum_{\{K\}} \phi_{\{K\}}^{(k)q}(k_1\cdots k_n)^z T_{\{K\}}^{(k)q}(k_1\cdots k_n)^z \ . \tag{49}$$

However, consistent with the idea that a pulse occurs on a time scale which is much faster than either relaxation or internal coupling processes, the spin density operator can also be written

$$\sigma = \prod_{i=1}^{n}\sigma_i = \sum_{\substack{k_i q_i \\ i=1,n}}^{2I_i} \mathcal{Y}^{(k_1)q_1}(I_1)\mathcal{Y}^{(k_2)q_2}(I_2)\cdots\mathcal{Y}^{(k_n)q_n}(I_n) \times \phi^{(k_1)q_1}\phi^{(k_2)q_2}\cdots\phi^{(k_n)q_n} \ . \tag{50}$$

It then follows that the relation between the two expansion coefficients in Eqs. (49) and (50) is

$$\phi_{\{K\}}^{(k)q}(k_1 k_2 \cdots k_n)^z = \sum_{\substack{q_i \\ i=1,n}} \langle k_1 q_1 k_2 q_2 \cdots k_n q_n | \times (k_1 k_2 \cdots k_n)^z \{K\} kq\rangle \phi^{(k_1)q_1}\phi^{(k_2)q_2}\cdots\phi^{(k_n)q_n} \ . \tag{51}$$

For time dependent fields of the type Eq. (14), the single spin result Eq. (26) can be used for each spin contribution $\phi^{(k_i)q_i}$ to Eq. (51).

In many treatments of relaxation problems, the effects of pulses are usually confined to the single spin dipolar polarization only. Effects of simultaneous spin polarizations and higher multipole polarizations are often ignored. However, as seen by Eq. (51), even when the spin density matrix factors, the pulse causes changes in all but the identity operator (i.e., $k = q = \{K\} = k_1 \cdots k_n = 0$). To see this, by means of an example, the explicit operators which completely span the 4×4 space of two spins of 1/2 can be written in terms of spherical components of the spin operators $\mathbf{I}_1$ and $\mathbf{I}_2$ for spins 1 and 2, respectively: identity:

$$T^{00}(00) = [(2I_1+1)(2I_2+1)]^{-1/2} \ ; \tag{52}$$

scalar:

$$T^{00}(11) \propto \mathbf{I}_1 \cdot \mathbf{I}_2 \ ; \tag{53}$$

vectors: $q = 0, \pm 1$:

(a) $T^{1q}(10) \propto I_1^q$ (54)

(b) $T^{1q}(01) \propto I_2^q$ (55)

(c) $T^{1q}(11) \propto (\mathbf{I}_1 \times \mathbf{I}_2)^{\infty}$, (56)

and second rank symmetric traceless tensor composed of $\mathbf{I}_1$ and $\mathbf{I}_2$,

$$T^{2q}(11) \propto [\mathbf{I}_1 \mathbf{I}_2]^{(2)q} \ . \tag{57}$$

The corresponding polarizations are given by Eq. (51) with the various appropriate values of k, q, k_1, and k_2. It is therefore seen that not only the vectors (a) and (b), but also the scalar polarization $\mathbf{I}_1 \cdot \mathbf{I}_2$, the cross product (c), and the second rank tensor polarizations are all affected by the pulse and are explicitly given by Eq. (51).

V. DISCUSSION

The time evolution of magnetic multipoles in the presence of a time-dependent vector magnetic field is shown in this paper to be particularly simple at resonance. In a spherical basis, the multipoles all transform as spherical harmonics with arguments $\omega_1\tau$ and $\omega_0\tau$. Since the Hamiltonian is only the Zeeman interaction between a vector magnetic field, Eqs. (1) and (14), it is expected that these simple results are valid for time scales which are typical of a state preparing pulse in NMR.

The resonance solutions show that the magnetic multipoles are simply rotated by the magnetic field. Hence the usual picture of a magnetic vector being pulsed away from its equilibrium value can be directly carried over to the higher multipoles. This is a consequence of the fact that, in the rotating frame, the magnetic field is constant at resonance, $\omega = \omega_0$ for multipoles of *all* tensor ranks up to the maximum $k = 2I$. The nonresonance solutions do not have this simplification because of additional coupling between the $2k+1$ components of each multipole. In both nonresonance and resonance cases, an interaction of the type Eq. (1) cannot lead to mixing between multipoles of different tensor rank.

On the other hand, for multispin systems, pulses lead to changes in a variety of mixed polarizations and higher multipoles. Correct theoretical treatment of spin relaxation phenomena should include these terms as initial conditions.

ACKNOWLEDGMENTS

The author is grateful for useful discussion with Dr. B. C. Eu. This research is funded by the National Sciences and Engineering Research Council of Canada (NSERC) and a grant from the Gouvernement du Québec.

APPENDIX

Using the following notations,

$$[\pm q] \equiv e^{i\Delta q t}\,\hat{\phi}_q^{(k)} \pm e^{-i\Delta q t}\,\hat{\phi}_{-q}^{(k)} \tag{A1}$$

and

$$[\pm \dot{q}] \equiv e^{i\Delta q t}\,\dot{\hat{\phi}}_q^{(k)} \pm e^{-i\Delta q t}\,\dot{\hat{\phi}}_{-q}^{(k)} \ , \tag{A2}$$

the first five derivatives of $\hat{\phi}_0^{(k)}$ are

$$\dot{\hat{\phi}}_0^{(k)} = \tfrac{1}{2} i\omega_1 \sqrt{k(k+1)}\,[+1] \ , \tag{A3}$$

$$\ddot{\hat{\phi}}_0^{(k)} + [\tfrac{1}{2}\omega_1^2 k(k+1)]\hat{\phi}_0^{(k)} = -\tfrac{1}{2}\omega_1\Delta\sqrt{k(k+1)}\,[-1] - \tfrac{1}{4}\omega_1^2\sqrt{k(k+1)(k-1)(k+2)}\,[+2] \ , \tag{A4}$$

$$\dddot{\hat{\phi}}_0^{(k)} + \{\tfrac{1}{2}\omega_1^2[k(k+1) + \tfrac{1}{2}(k-1)(k+2)] + \Delta^2\} \times \dot{\hat{\phi}}_0^{(k)} = A_3[-2] + B_3[+3], \tag{A5}$$

where

$$A_3 = -i\,\tfrac{3}{4}\Delta\omega_1^2\sqrt{k(k+1)(k-1)(k+2)} \ , \tag{A6}$$

$$B_3 = -i\,\tfrac{1}{8}\omega_1^3\sqrt{k(k+1)(k-1)(k+2)(k-2)(k+3)} \ , \tag{A7}$$

$$\ddddot{\hat{\phi}}_0^{(k)} + \{\tfrac{1}{2}\omega_1^2[k(k+1) + \tfrac{1}{2}(k-1)(k+2)] + \Delta^2\}\ddot{\hat{\phi}}_0^{(k)} = A_4[-1] + B_4[+2] + C_4[-3] + D_4[+4] \ , \tag{A8}$$

where

$$A_4 = \tfrac{3}{8}\omega_1^3\Delta\sqrt{k(k+1)}\,(k-1)(k+2) \ , \tag{A9}$$

$$B_4 = \tfrac{1}{2}\omega_1^2\sqrt{k(k+1)(k-1)(k+2)}\,(3\Delta^2 + \tfrac{1}{8}\omega_1^2(k-2)(k+3)) \ , \tag{A10}$$

$$C_4 = \tfrac{3}{4}\omega_1\Delta^3\sqrt{k(k+1)(k-1)(k+2)(k-2)(k+3)} \ , \tag{A11}$$

$$D_4 = \tfrac{1}{16}\omega_1^4\sqrt{k(k+1)(k-1)(k+2)(k-2)(k+3)(k-3)(k+4)} \ , \tag{A12}$$

$$\overset{\cdot\cdot\cdot\cdot\cdot}{\hat{\phi}}{}_0^{(k)} + \{\tfrac{1}{2}\omega_1^2[k(k+1) + \tfrac{1}{2}(k-1)(k+2)] + \Delta^2\}\dddot{\hat{\phi}}_0^{(k)} - \tfrac{1}{4}\omega_1^2(k-1)(k+2)[9\Delta^2 + \tfrac{1}{4}\omega_1^2(k-2)(k+3)]\dot{\hat{\phi}}_0^{(k)} = A_5[-2] + B_5[+3] + C_5[-4] + D_5[+5] \ , \tag{A13}$$

where

$$A_5 = [B_4(2i\Delta) + A_4(\tfrac{1}{2}i\omega_1)\sqrt{(k-1)(k+2)} + C_4(\tfrac{1}{2}i\omega_1)\sqrt{(k-2)(k+3)}\,] \ , \tag{A14}$$

$$B_5 = [C_4(3i\Delta) + B_4(i\omega_1)\sqrt{(k-2)(k+2)} + D_4(\tfrac{1}{2}i\omega_1)\sqrt{(k-3)(k+4)}\,] \tag{A15}$$

$$C_5 = [D_4(4i\Delta) + C_4(\tfrac{1}{2}i\omega_1)\sqrt{(k-3)(k+4)}\,] \ , \tag{A16}$$

and

$$D_5 = D_4(\tfrac{1}{2}i\omega_1)\sqrt{(k-4)(k+5)} \ . \tag{A17}$$

For $k = 1$, these equations reduce to

$$\dddot{\hat{\phi}}_0^{(1)} + \Omega^2\dot{\hat{\phi}}_0^{(1)} = 0 \ , \tag{A18}$$

while for $k = 2$, to

$$\overset{\cdot\cdot\cdot\cdot\cdot}{\hat{\phi}}{}_0^{(2)} + 5\Omega^2\dddot{\hat{\phi}}_0^{(2)} + 4\Omega^4\dot{\hat{\phi}}_0^{(2)} = 0 \ . \tag{A19}$$

Using the initial conditions Eq. (33), it is seen that the odd derivatives vanish and the even derivatives are given by Eqs. (36) and (37).

Higher derivatives can be obtained by using the relation

$$[\pm\dot{q}] = (\tfrac{1}{2}i\omega_1)\sqrt{(k-q)(k+q-1)}\,[\pm(q+1)] + (\tfrac{1}{2}i\omega_1)\sqrt{(k+q)(k-q+1)}\,[\pm(q-1)] \tag{A20}$$

to remove the derivatives of $\hat{\phi}_q^{(k)}$ for $q \neq 0$.

[1]See, for example, D. Shaw, *Fourier Transform NMR Spectroscopy* (Elsevier, Amsterdam, 1976).
[2]B. C. Sanctuary, Phys. Rev. A **20**, 1169 (1979).
[3]J. A. R. Coope and R. F. Snider, J. Math. Phys. **11**, 1103 (1970); J. A. R. Coope, *ibid*. **11**, 1591 (1970). See also Appendix A of F. M. Chen, H. Moraal and R. F. Snider, J. Chem. Phys. **57**, 542 (1972).
[4]B. C. Sanctuary, J. Chem. Phys. **64**, 4352 (1976).
[5]I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals Series and Products* (Academic, New York, 1965), Eq. (8.733.1). Note that the associated Legendre functions, $P_k^q(x)$ of Gradshteyn and Ryzhik differ by $(-1)^q$ from those defined by A. E. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U.P., Princeton, NJ, 1960). The spherical harmonics used here are those defined by Edmonds.
[6]R. D. Hight, R. T. Robiscoe, and W. R. Thorson, Phys. Rev. A **15**, 1079 (1977).
[7]A. P. Yutsis, I. B. Levinson, and V. V. Vanagas, *The Theory of Angular Momentum* (Israel Program for Scientific Translations, Washington DC, 1962).