Magnetic multipoles in nonresonance time dependent fields

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The time dependence of the density operator for an arbitrary number of uncoupled spins in a resonant field has recently been presented [B. C. Sanctuary, J. Chem. Phys. 73, 1048(1980). In this paper, the solutions are extended to the nonresonant case and are given in terms of rotation matrices.

In this paper, we present the complete analytic solution for the time evolution of a multispin system under the influence of a Zeeman Hamiltonian.

In a recent publication[1] one of us considered the effect of a time dependent magnetic field,

$$\mathrm{H}(t)=\hat{x}\tilde{H}_1(\omega)\cos\omega t-\hat{y}\tilde{H}_1(\omega)\sin\omega t+H_0\hat{z} \tag{1}$$

on a multispin system. Since the duration of the applied field was taken as short (typical of pulses in nuclear magnetic relaxation studies), the effects of spin couplings and relaxation can be ignored so that the Hamiltonian is taken as

$$\mathcal{H}=-\hbar\sum^{n}\gamma_i \mathrm{I}_i\cdot \mathrm{H}(t)\ . \tag{2}$$

The treatment in Ref. 1 gives the spin density matrix for the multispin system in terms of magnetic multipoles (see Refs. 1 and 2)

$$\sigma=\sum_{kq}\sum_{\substack{k_i\\ i=1,n}}^{2I_i}\sum_{\{K\}}\phi_{\{K\}}^{(k)q}(k_1\cdots k_n)^Z\,T_{\{K\}}^{(k)q}(k_1\cdots k_n)^Z\ , \tag{3}$$

where, since the spins are not coupled on the pulse time scale, the spin polarizations are given by

$$\phi_{\{K\}}^{(k)q}(k_1k_2\cdots k_n)^Z=\sum_{\substack{q_i\\ i=1,n}}\langle k_1q_1k_2q_2\cdots k_nq_n|(k_1k_2\cdots k_n)^Z\{K\}kq\rangle \times\phi^{(k_1)q_1}\phi^{(k_2)q_2}\cdots\phi^{(k_n)q_n}\ , \tag{4}$$

where the transformation matrix is an n-j symbol.[3] In particular, $\phi^{(k)q}=\phi_q^{(k)*}$ is the single spin multipole polarization.

In order to solve the relaxation equations for multispin systems, the initial nonequilibrium state must be specified. Reference 1 addressed this problem. Before the pulse, it is assumed that all the spins are at equilibrium in a large static magnetic field in the z direction, or

$$\phi_q^{(k)}(0)=\delta_{q,0}\ . \tag{5}$$

The field, Eq. (1), is then applied for a time τ and the multispin polarization $\phi_{\{K\}}^{(k)q}(k_1k_2\cdots k_n)^Z$ at time τ is given by Eq. (4) if the single spin polarizations, $\phi_q^{(k)}(\tau)$ are known. These single spin multipoles, $\phi^{(k)}(\tau)$, for different spins, I_i, have the same time dependence in the magnetic field $\mathrm{H}(t)$ *except* for the value of the gyromagnetic ratio γ_i. This is a consequence of the Zeeman Hamiltonian (see Ref. 1 for details). The results below are valid for any value of γ_i and we suppress the subscript i.

In Ref. 1, both on-resonance and nonresonance pulses are considered. The resonance solution is obtained when the Larmour precession frequency, $\omega_0=\gamma H_0$ is equal to the applied frequency ω, Eq. (1). In this case, the solutions normalized to Eq. (5) are

$$\phi_q^{(k)}(\tau)=(i)^q\left(\frac{(k-q)!}{(k+q)!}\right)^{1/2}P_k^q(\cos\omega_1\tau)\,e^{iq\omega_0\tau}\ , \tag{6}$$

where P_k^q are the associated Legendre functions defined by Edmonds[4] and

$$\omega_1=\gamma\tilde{H}_1(\omega)\ . \tag{7}$$

The nonresonance solutions, $\omega\neq\omega_0$, were not found in general in Ref. 1 although the cases $k=1$ and 2 were obtained and a method was outlined for finding the others. In this paper we report the full solution valid for all the multipoles both on and off resonance. This is accomplished by using the fact that the behavior of a spin, I, when acted upon by a Zeeman Hamiltonian, always corresponds to a physical rotation of the angular momentum in three-dimensional space.[5] Therefore, if the spin state is given as a superposition

$$\psi(\tau)=\sum_M A_M^I(\tau)|IM\rangle \tag{8}$$

with initial conditions $A_M^I(0)$, then the coefficients, $A_M^I(\tau)$, evolve as

$$A_M^I(\tau)=\sum_N \mathfrak{D}_{MN}^{(I)}(\alpha\beta\gamma)A_N^I(0)\ , \tag{9}$$

where $\mathfrak{D}^{(I)}(\alpha\beta\gamma)$ is a rotation matrix[4] and the Euler angles are time dependent.

For the special case that only one state is initially populated, i.e., $A_M^I(0)=\delta_{MF}$ the pure single spin density operator is given for all times by

$$\sigma_{MM'}(\tau)=A_M^I(\tau)A_{M'}^{I*}(\tau)=\mathfrak{D}_{MF}^{(I)}(\alpha\beta\gamma)\,\mathfrak{D}_{M'F}^{(I)*}(\alpha\beta\gamma)\ . \tag{10}$$

Using Eq. (7) of Ref. 1, the *unnormalized* single spin polarizations are given by

$$\phi^{(k)q}=\sum_{MM'=-I}^{I}(2I+1)^{1/2}\times(-1)^{I-M'}(2k+1)^{1/2}\begin{pmatrix} I & k & I\\ -M & -q & M'\end{pmatrix}\sigma_{MM'}^{I}\ , \tag{11}$$

where $\sigma_{MM'}^I=\langle IM|\sigma|IM'\rangle$.

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Using the property of rotation matrices, Eq. (4.3.2.) of Ref. 4 and the orthogonality of 3-j coefficients, Eq. (11) with Eq. (10) becomes

$$\phi_q^{(k)} = (2I+1)^{1/2}(2k+1)^{1/2}(-1)^{I-F}\mathfrak{D}_{q,0}^{(k)}(\alpha\beta\gamma)\begin{pmatrix} I & I & k \\ F & -F & 0 \end{pmatrix} . \quad (12)$$

Finally, imposing the condition Eq. (5) gives the normalized solutions as

$$\phi_q^{(k)}(\tau) \equiv \mathfrak{D}_{q,0}^{(k)}(\alpha\beta\gamma) = \left(\frac{(k-q)!}{(k+q)!}\right)^{1/2} P_k^q(\cos\beta)\, e^{iq\alpha} . \quad (13)$$

This solution has the same form as the resonance solution Eq. (6), but is valid both on and off resonance. It should be noted that the Euler angle γ is not relevant for this problem because only the $q=0$ component of the $\mathfrak{D}^{(k)}$ matrix is required to obtain the time dependence of $\phi_q^{(k)}(t)$.

The Euler angles are independent of the spin I. Therefore, it is only necessary to solve the spin $I=\frac{1}{2}$ case in order to determine the time dependence of the angles β and α. This solution is well known[6,7] in terms of the vector polarizations $\phi^{(1)}$, namely,

$$\phi_0^{(1)} = \cos\beta = \frac{1}{\Omega^2}\left[\omega_1^2\cos(\Omega\tau) + (\omega_0-\omega)^2\right] \quad (14)$$

and

$$\begin{aligned} \phi_-^{(1)} &\equiv \phi_x^{(1)} - i\phi_y^{(1)} = -\sin\beta\exp(i\alpha) \\ &= +\frac{\omega_1^3}{2\Omega^2}\exp(+i\omega_0\tau)\left(\frac{\exp\{-i[\Omega-(\omega-\omega_0)]\tau\}}{\Omega-(\omega-\omega_0)}\right. \\ &\quad \left. - \frac{\exp\{+i[\Omega+(\omega-\omega_0)]\tau\}}{\Omega+(\omega-\omega_0)} - \frac{2(\omega-\omega_0)}{\omega_1^2}\exp[+i(\omega-\omega_0)\tau]\right), \end{aligned} \quad (15)$$

where

$$\Omega = [\omega_1^2 + (\omega_0-\omega)^2]^{1/2} . \quad (16)$$

Equation (15) along with Eq. (14) can be used to determine the angle $\alpha(t)$. A simpler expression for $\alpha(t)$ could not be found. However, at resonance, $\omega=\omega_0$, these equations reduce to give

$$\beta = \omega_1\tau, \quad \alpha = \omega_0\tau + \tfrac{1}{2}\pi \quad (17)$$

in agreement with Eq. (6).

In nuclear magnetic relaxation experiments, the standard method of preparing the state is by the use of pulses. In spite of the fact that the effect of a pulse on a magnetic vector is well known, in multispin systems the full density matrix is needed in order to describe the nonequilibrium state of the system, which is produced by a state preparing pulse acting on a system initially at equilibrium in a large static magnetic field. The determination of the initial state is essential for the description of spin relaxation phenomena in multispin systems.

For the case of a Zeeman Hamiltonian, Eq. (2), the full density matrix can be calculated using Eqs. (3) and (4) along with the solutions Eq. (12) normalized to the initial equilibrium value of $\phi_q^{(k)}$ (see Ref. 1) and the Euler angles α, β, which are given by Eqs. (14) and (15) for resonance and nonresonance conditions.

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