Dynamics of single spin systems under arbitrary amplitude modulated fields

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Using a spherical tensor operator basis a general method of solution to the time evolution of the spin density matrix for a spin of arbitrary magnitude I is given. Rather than using time ordering techniques, we present an integral equations approach for calculating the effects of arbitrary pulse shapes. The method is shown to provide a rapidly converging perturbation expansion which is useful in explaining many pulse shapes. In particular, a simple recipe for the calculation of the magnetization results from this technique. The successive terms in the perturbation expansion avoid multiple commutators such as are encountered in the Magnus expansion of the propagator. These terms are given simply as integrals of the pulse shape function. The examples of the Bloch–Siegert problem and the exact dynamics of a spin interacting with a rotating rf field combined with an isotropic relaxation and a regeneration mechanism are presented in the context of the method of transformations in Liouville space.

I. INTRODUCTION

The essence of this work is the use of the spherical tensor operators, involved in the decomposition of the spin density matrix, in the formulation of a general method of solution to problems in NMR involving arbitrary magnetic radiation fields. Experiments involving nonrotating fields have been performed.[1] In addition, pulse shape analysis and frequency response are vital aspects of current NMR with particular relevance to MRI. Our study attempts to provide a means of explanation of such experiments which are now feasible with the advanced technology of pulse generators. One of the oldest examples of pulse modulation is that of a linearly polarized field[2] and we study this problem in detail (see Appendix B).

The conventional treatment of time-dependent problems in NMR (or in quantum mechanics) is to study the equation of motion for the time-evolution operator $U(t)$:

$$i\hbar \frac{\partial}{\partial t} U(t) = \mathscr{H}(t)U(t), \quad U(0) = 1. \tag{1}$$

One formal solution to Eq. (1) is the Feynman–Dyson expansion[3]

$$U(t) = T\exp\left\{ -\frac{i}{\hbar}\int_0^t \mathscr{H}(t')dt' \right\}, \tag{2}$$

where T denotes the time-ordering operator. This expansion, however, as pointed out in the past[4] has the disadvantages of not preserving the unitary nature of $U(t)$ upon truncation of the series and is usually accurate for a small time interval. An alternate solution to Eq. (1) is the Magnus[5] expansion

$$U(t) = \exp\{\Omega(t)\}, \quad \Omega(0) = 0 \tag{3}$$

with

$$\Omega(t) = \sum_{n=0}^{\infty} \Omega^{(n)}(t), \tag{4}$$

where the first few terms are

$$\Omega^{(0)}(t) = \frac{-i}{\hbar}\int_0^t \mathscr{H}(t_1)dt_1,$$

$$\Omega^{(1)}(t) = \frac{-1}{2}\left(\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 [\mathscr{H}(t_2),\mathscr{H}(t_1)],$$

$$\Omega^{(2)}(t) = \frac{-1}{6}\left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \times([\mathscr{H}(t_3),[\mathscr{H}(t_2),\mathscr{H}(t_1)]] + [[\mathscr{H}(t_3),\mathscr{H}(t_2)],\mathscr{H}(t_1)]), \quad \text{etc.} \tag{5}$$

This expansion preserves the unitarity of $U(t)$ upon truncation of the series (4) since all of the terms $\Omega^{(n)}(t)$ are anti-Hermitian. This feature, as well as faster convergence for small times, suggests that the Magnus formula is more useful than the form in Eq. (2). Light[4] has also stated that the nth term in the Magnus expansion is just as simple and often simpler to evaluate than the corresponding term in the perturbation expansion series (2). Like all expansions, however, the Magnus formula has some disadvantages; one being the necessity to perform multiple commutators and subsequently to evaluate the exponential operator either by expanding the exponential or by diagonalizing the exponent $\Omega(t)$ in Eq. (3) to finally arrive at the propagator $U(t)$.

The Magnus expansion can, however, sometimes be reduced to a simplified form when the Hamiltonian operator $\mathscr{H}(t)$ is expressible in terms of the generators X_i of a finite n-dimensional Lie algebra

$$\mathscr{H}(t) = \sum_{i=1}^{n} h_i(t)X_i. \tag{6}$$

For these cases the exponent $\Omega(t)$ must then also be a linear combination of the Lie elements[6]

$$\Omega(t) = \sum_{i=1}^{n} \Omega_i(t)X_i. \tag{7}$$

By substituting Eqs. (6) and (7) into Eqs. (1) and (3) and employing the identity[6]

$$\frac{\partial}{\partial \lambda} e^{Z(\lambda)} = \int_0^1 dx\, e^{xZ} Z'(\lambda) e^{-xZ} e^{Z} \tag{8}$$

and the similarity transformation

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$$e^{x\Omega}X_i\, e^{-x\Omega} = \sum_{j=1}^{n} g_{ij}(x)X_j, \tag{9}$$

as well as the closure property of the generators of the Lie algebra, then the Magnus expansion problem reduces into an nth order system of differential equations[7]:

$$\frac{-i}{\hbar} h_j(t) = \sum_{i=1}^{n} \left\{\int_0^1 g_{ij}(x)dx\right\} \dot{\Omega}_i(t), \quad j = 1,2,...,n. \tag{10}$$

By inverting Eq. (10) one gets a set of nonlinear differential equations in the $\Omega_i(t)$ which have been solved exactly for certain algebras.[6] For these restricted Lie algebras, the Magnus expansion is then a very useful result in obtaining closed-form solutions to time-dependent problems (these include the cases for which the multiple commutator converges to a c number).

In NMR, the algebra is that of the angular momentum operators $\{I_x, I_y, I_z\}$ so that any amplitude-modulated magnetic field Hamiltonian is expressed in the same form as Eq. (6), i.e.,

$$\begin{aligned}\mathscr{H}(t) &= -\boldsymbol{\mu}(t)\cdot\mathbf{I}\\ &= -[\mu_x(t)I_x + \mu_y(t)I_y + \mu_z(t)I_z],\end{aligned} \tag{11}$$

where $\boldsymbol{\mu}(t)$ is the magnetic moment of the spin I. The exponent $\Omega(t)$ is then given by [cf. Eq. (7)]

$$\Omega(t) = \alpha(t)I_x + \beta(t)I_y + \gamma(t)I_z \tag{12}$$

and the analogous equations to Eq. (10) are

$$\begin{aligned}\frac{i}{\hbar}\mu_x(t) &= \frac{\dot{R}}{2R}\alpha\left[1 - \frac{\sinh\sqrt{R}}{\sqrt{R}}\right] + \dot{\alpha}\frac{\sinh\sqrt{R}}{\sqrt{R}}\\ &\quad + i\frac{(\beta\dot{\gamma} - \gamma\dot{\beta})}{R}[\cosh\sqrt{R} - 1],\\ \frac{i}{\hbar}\mu_y(t) &= \frac{\dot{R}}{2R}\beta\left[1 - \frac{\sinh\sqrt{R}}{\sqrt{R}}\right] + \dot{\beta}\frac{\sinh\sqrt{R}}{\sqrt{R}}\\ &\quad + i\frac{(\dot{\alpha}\gamma - \alpha\dot{\gamma})}{R}[\cosh\sqrt{R} - 1],\\ \frac{i}{\hbar}\mu_z(t) &= \frac{\dot{R}}{2R}\gamma\left[1 - \frac{\sinh\sqrt{R}}{\sqrt{R}}\right] + \dot{\gamma}\frac{\sinh\sqrt{R}}{\sqrt{R}}\\ &\quad + i\frac{(\alpha\dot{\beta} - \dot{\alpha}\beta)}{R}[\cosh\sqrt{R} - 1]\end{aligned} \tag{13}$$

subject to the boundary conditions

$$\alpha(0) = \beta(0) = \gamma(0) = 0, \tag{14}$$

where

$$R(t) \equiv \alpha(t)^2 + \beta(t)^2 + \gamma(t)^2. \tag{15}$$

It is apparent that the set of nonlinear equations (13) in α, β, and γ can only be solved numerically when the magnetic moment (or field) components are complicated functions in time t. Consequently, the Magnus expansion approach to general amplitude-modulated problems in NMR is practical only in the perturbation form given by Eqs. (3), (4), and (5). In fact, NMR pulse shape analysis is frequently studied perturbatively using an average Hamiltonian expansion.[8]

This paper concentrates on the development of a complementary solution to general amplitude-modulated radiation field problems in NMR. From the Liouville equation, an integral equation approach is developed which describes the time evolution of the NMR observables, for any spin magnitude I, for arbitrary pulse shapes. We show that the formal solution to the integral equation provides a perturbation expansion for the calculation of arbitrary field effects. In fact, the successive terms in the expansion are iterated integrals of the kernel function $K(t,t')$ which fully characterizes the specific modulation problem. The NMR signal is thus just an infinite sum of multiple integrals of the characteristic kernel function $K(t,t')$. These integrals are no more complicated than the corresponding integrals of the n-fold multiple commutators of $\mathscr{H}(t')$ which make up the exponent operator $\Omega(t)$ in the Magnus expansion. That is, the integrals are essentially n-fold iterated integrals of the pulse shape function $\omega_1(t)$. Our treatment consists of evaluating these multiple integrals which make up the perturbation solution. In the Magnus expansion, however, one must evaluate not only similar multiple integrals but also a multiple commutator for every such multiple integral to obtain the functional $\Omega(t)$. The NMR signal must then be obtained after evaluating the exponential operator $\exp[\Omega(t)]$ and tracing out the relevant observable.

It is also found that our expansion converges rapidly not only for well-behaved simple pulse shapes with any value of the resonance offset but also for any complex pulse shape far from resonance. In fact, convergence is just as good as in the Magnus expansion series since our series of iterated integrals of $K(t,t')$ parallels that of the exponent operator $\Omega(t)$. This then has the advantage of explaining general pulse shape effects where one need only retain the first few terms in the expansion. We use this to describe the effects of $\sin(\omega_c t)/t$ and Gaussian pulse envelopes.

By exploiting the Lie algebra in the quantum Liouville equation, we therefore create a perturbation expansion which is completely free of operators. In the same spirit, the Bloch–Siegert problem and an optical pumping problem with isotropic relaxation are analyzed by the method of operator-free transformations in Liouville space. These illustrate how a technique of constant and frequency-modulated rotating frames can be used in the framework of a spherical tensor basis to solve the spin density matrix without recourse to a perturbation expansion. Such results are presented in Appendices B and C.

II. THEORY

Using a single spin spherical tensor basis[9,10] the spin density matrix is calculated by solving the quantum Liouville equation for a Hamiltonian $\mathscr{H}$,

$$i\hbar\frac{d}{dt}\sigma(t) = [\mathscr{H},\sigma(t)]. \tag{16}$$

The density matrix for a spin of arbitrary magnitude I is expanded in the multipole basis,

$$\sigma(t) = \frac{1}{2I+1}\left[E_I + \sum_{k=1}^{2I}\sum_{q=-k}^{k}\phi_q^k(t)\mathscr{Y}^{(k)q}(\mathbf{I})\right], \tag{17}$$

so the complete properties of the spin system are determined by the polarizations $\phi_q^k(t) = \langle\mathscr{Y}^{(k)q\dagger}\rangle$ which are expectation values of the multipole operators. Using the orthogonality of the operator basis these are governed by the set of first order coupled differential equations:

$$\dot{\phi}_q^k(t) = \frac{1}{2I+1} \sum_{k'q'} \left\langle\left\langle \mathscr{Y}^{(k)q} \middle| \frac{-i}{\hbar} [\mathscr{H}, \mathscr{Y}^{(k')q'}] \right\rangle\right\rangle \phi_{q'}^{k'}(t). \tag{18}$$

where the inner product is

$$\langle\langle \mathscr{Y}^{(k)q} | A | \mathscr{Y}^{(k')q'} \rangle\rangle \equiv \mathrm{Tr}\{\mathscr{Y}^{(k)q\dagger} A \mathscr{Y}^{(k')q'}\}. \tag{19}$$

A is any spin operator and dagger is the Hermitian adjoint. Some of the useful properties of the $\mathscr{Y}^{(k)q}$'s are listed in Appendix A. Using the expansion (A2), the transition probabilities $|IM'\rangle$ to $|IM\rangle$ multiquantum transitions are given by

$$P^I_{M'\to M}(t) = |\langle |IM\rangle\langle IM'|\rangle|^2 = \frac{1}{2I+1} \left| \sum_{kq} (i)^k (2k+1)^{1/2} \times \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} \phi_q^k(t) \right|^2. \tag{20}$$

In interpreting the NMR experiments the observables are given by the components of the vector magnetization:

$$\langle I_z \rangle = -i \sqrt{\frac{I(I+1)}{3}} \langle \mathscr{Y}^{(1)0}(\mathbf{I}) \rangle = i \sqrt{\frac{I(I+1)}{3}} \phi_0^1, \tag{21}$$

$$\langle I_x \rangle = i \sqrt{\frac{I(I+1)}{6}} (\langle \mathscr{Y}^{(1)1} \rangle - \langle \mathscr{Y}^{(1)-1} \rangle) = i \sqrt{\frac{I(I+1)}{6}} (\phi_1^1 - \phi_{-1}^1), \tag{22}$$

and

$$\langle I_y \rangle = \sqrt{\frac{I(I+I)}{6}} (\langle \mathscr{Y}^{(1)1} \rangle + \langle \mathscr{Y}^{(1)-1} \rangle) = \sqrt{\frac{I(I+I)}{6}} (\phi_1^1 + \phi_{-1}^1). \tag{23}$$

If we consider a Zeeman interaction

$$\mathscr{H}(t) = -\gamma\hbar \mathbf{H}(t)\cdot\mathbf{I}, \tag{24}$$

where the magnetic field is chosen quite generally as

$$\mathbf{H}(t) = H_x(t)\cos(\omega t - \phi)\hat{x} - H_y(t)\sin(\omega t - \phi)\hat{y} + H_0\hat{z}, \tag{25}$$

then in spherical tensor form

$$\mathscr{H}(t) = i\hbar\omega_0 \sqrt{\frac{I(I+1)}{3}} \mathscr{Y}^{(1)0}(\mathbf{I}) - i\hbar\omega_1(t) e^{i(\omega t - \phi)} \sqrt{\frac{I(I+1)}{6}} \mathscr{Y}^{(1)1}(\mathbf{I}) + i\hbar\omega_{-1}(t) e^{-i(\omega t - \phi)} \sqrt{\frac{I(I+1)}{6}} \mathscr{Y}^{(1)-1}(\mathbf{I}) \tag{26}$$

is the Hamiltonian defining the problem where

$$\omega_0 = \gamma H_0 \text{ (Larmor frequency)} \tag{27}$$

and

$$\omega_{\pm 1}(t) = \gamma H_{\pm 1}(t) = \gamma[H_x(t)\cos(\omega t - \phi) \pm i H_y(t)\sin(\omega t - \phi)] e^{\mp i(\omega t - \phi)}. \tag{28}$$

It is noted that in contrast to the pure rotating field a time dependence of a general form is attached to the field components H_x and H_y. The quantity $\omega_{\pm 1}(t)$ of Eq. (28) is hence a modulated rf frequency of arbitrary form.

Substituting Eq. (26) into Eq. (18) gives again a set of first order coupled differential equations

$$\dot{\hat{\phi}}_q^k(t) = i\frac{\omega_1(t)}{2} e^{i\Delta\omega t} \sqrt{(k+q)(k-q+1)} \hat{\phi}_{q-1}^k(t) + \frac{i\omega_{-1}(t)}{2} e^{-i\Delta\omega t} \sqrt{(k-q)(k+q+1)} \hat{\phi}_{q+1}^k(t), \tag{29}$$

where the phase-shifted Larmor rotating frame

$$\hat{\phi}_q^k(t) = \exp[-iq(\omega_0 t - \phi)] \phi_q^k(t) \tag{30}$$

has been defined.

A. Integral equations approach to amplitude-modulation analysis

The method of solution rests upon obtaining an integral equation for the polarizations $\hat{\phi}_q^k$ starting from Eq. (29). For $k = 1$ (i.e., the NMR observables ϕ_q^1) we have

$$\dot{\hat{\phi}}_1^1(t) = i\frac{\omega_1(t)}{\sqrt{2}} e^{i\Delta\omega t} \hat{\phi}_0^1(t), \tag{31}$$

$$\dot{\hat{\phi}}_0^1(t) = i\frac{\omega_{-1}(t)}{\sqrt{2}} e^{-i\Delta\omega t} \hat{\phi}_1^1(t) + i\frac{\omega_1(t)}{\sqrt{2}} e^{i\Delta\omega t} \hat{\phi}_{-1}^1(t), \tag{32}$$

$$\dot{\hat{\phi}}_{-1}^1(t) = i\frac{\omega_{-1}(t)}{\sqrt{2}} e^{-i\Delta\omega t} \hat{\phi}_0^1(t). \tag{33}$$

Integrating Eqs. (31) and (33) from an initial time $t = 0$ to time t gives

$$\hat{\phi}_{\pm 1}^1(t) = \hat{\phi}_{\pm 1}^1(0) + \frac{i}{\sqrt{2}} \int_0^t \omega_{\pm 1}(t') e^{\pm i\Delta\omega t'} \hat{\phi}_0^1(t') dt'. \tag{34}$$

Substituting Eq. (34) into Eq. (32) and integrating both sides of the equation (and reversing integration order) gives the integral equation

$$\hat{\phi}_0^1(t) = \hat{\phi}_0^1(0) + W_{-1}(t)\hat{\phi}_1^1(0) + W_{+1}(t)\hat{\phi}_{-1}^1(0) + \int_0^t K(t,t')\hat{\phi}_0^1(t')dt', \tag{35}$$

where

$$W_{\pm 1}(t) = \frac{i}{\sqrt{2}} \int_0^t \omega_{\pm 1}(t') e^{\pm i\Delta\omega t'} dt'. \tag{36}$$

The kernel is identified as

$$K(t,t') = -\mathrm{Re}\left\{\omega_{+1}(t') e^{i\Delta\omega t'} \int_{t'}^t \omega_{+1}^*(\bar{t}) e^{-i\Delta\omega \bar{t}} d\bar{t}\right\}, \tag{37}$$

where Re denotes the real part and $*$ the complex conjugate.

The form obtained for the polarization $\hat{\phi}_0^1(t)$ [Eq. (35)] is an inhomogeneous linear Volterra integral equation of the second kind,[12] with kernel $K(t,t')$. The polarizations $\phi_1^1(t)$ and $\phi_{-1}^1(t)=\phi_1^{1*}(t)$ are subsequently obtained by integrating Eq. (34). Hence, for any general field modulation $\omega_1(t)$ the evolution of the NMR observables $\phi_q^1(t)$ is completely given by the solution of Eq. (35). Stated otherwise, the time evolution of the magnetizations of a spin of arbitrary magnitude I is completely determined from the properties of the kernel $K(t,t')$ of the integral equation (35). It is remarked that integral equations similar to Eq. (35) for $2\leqslant k\leqslant 2I$ are not as easily obtainable and we henceforth restrict calculations of the density matrix to $k=1$ ($q=-1,0,1$) for arbitrary spin I.

B. Properties of the kernel $K(t,t')$

Assuming the field modulation $\omega_1(t)$ to be a continuous function of t then $K(t,t')$ [Eq. (37)] is a continuous real-valued function on the rectangle R: $a\leqslant t\leqslant b$ and $a\leqslant t'\leqslant b$ ($a,b\in\mathbb{R}$) and bounded in R, $|K(t,t')|\leqslant M$ for some $M\in\mathbb{R}$. Piecewise discontinuous functions, such as step or heaviside functions, can also be treated over appropriately restricted time ranges. From a well-known theorem[13] for integral equations, the solution of $\phi_0^1(t)$ for $\phi_0^1(t)$ continuous in the interval $a\leqslant t\leqslant b$ is given formally by the Neumann series

$$\hat{\phi}_0^1(t)=\hat{\phi}_0^1(0)+W_{+1}(t)\hat{\phi}_{-1}^1(0)+W_{-1}(t)\hat{\phi}_1^1(0)+\int_0^t\Gamma(t,t')\{\hat{\phi}_0^1(0)+W_{+1}(t')\hat{\phi}_{-1}^1(0)+W_{-1}(t')\hat{\phi}_1^1(0)\}dt', \tag{38}$$

where the resolvent kernel $\Gamma(t,t')$ is given by

$$\Gamma(t,t')=\sum_{n=1}^{\infty}K^n(t,t') \tag{39}$$

with

$$K^1(t,t')=K(t,t'), \tag{40}$$

$$K^2(t,t')=\int_{t'}^{t}K(t,t'')K(t'',t')dt'', \tag{41}$$

$$K^3(t,t')=\int_{t'}^{t}K(t,t'')K^2(t'',t')dt'', \tag{42}$$

$$\vdots$$

$$K^n(t,t')=\int_{t'}^{t}K(t,t'')K^{n-1}(t'',t')dt''. \tag{43}$$

We observe that a closed-form expression for the resolvent $\Gamma(t,t')$ gives an immediate closed-form solution to Eq. (35). But $\Gamma(t,t')$ is in turn dependent on the iterated expressions (43) whose generalizability for all integer $n\geqslant 1$ is solely dependent on the analytic form of $K(t,t')$. The readiness with which a closed-form solution of Eq. (35) is obtainable, therefore, depends entirely on the kernel form. For example, if the kernel is a function of the difference $t-t'$:

$$K(t,t')=g(t-t'), \tag{44}$$

then the Laplace–Faltung theorem can be invoked on Eq. (35) giving an integral representation for $\phi_0^1(t)$:

$$\hat{\phi}_0^1(t)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{e^{st}}{1-G(s)}\times\left\{\frac{\hat{\phi}_0^1(0)}{s}+\overline{W}_{+1}(s)\hat{\phi}_{-1}^1(0)-\overline{W}_{+1}^*(s)\hat{\phi}_1^1(0)\right\}ds, \tag{45}$$

$$G(s)=\mathscr{L}[g][s]=\int_0^\infty g(t)e^{-st}dt, \tag{46}$$

and

$$\overline{W}_{+1}(s)=\mathscr{L}[W_{+1}][s]=\int_0^\infty W_{+1}(t)e^{-st}dt. \tag{47}$$

{$\mathscr{L}[f][s]$ denotes Laplace transform of f and $\mathscr{L}^{-1}[f](t)$ the inverse Laplace transform of f at s.} The pure rectangular pulse Hamiltonian (when H_x and H_y are constant in time) gives rise to such a treatment where the kernel can be identified from Eq. (37) as

$$K(t,t')=\begin{cases}-\dfrac{\omega_1^2}{\Delta\omega}\sin\Delta\omega(t-t'), & \Delta\omega\neq 0\\ -\omega_1^2(t-t'), & \Delta\omega=0\end{cases} \tag{48}$$

along with

$$W_{\pm 1}(t)=\begin{cases}\dfrac{\omega_1}{\sqrt{2}\Delta\omega}(e^{\pm i\Delta\omega t}-1), & \Delta\omega\neq 0\\ \pm i\dfrac{\omega_1 t}{\sqrt{2}}, & \Delta\omega=0\end{cases}. \tag{49}$$

Taking Laplace transforms it is found that

$$G(s)=-\frac{\omega_1^2}{s^2+\Delta\omega^2} \tag{50}$$

and

$$\overline{W}_{\pm 1(s)}=\pm\frac{i\omega_1}{\sqrt{2}s(s\mp i\Delta\omega)}. \tag{51}$$

Substituting Eqs. (50) and (51) into Eq. (45) gives immediately

$$\hat{\phi}_0^1(t)=-\frac{\omega_1}{\sqrt{2}\Omega^{(-)}}\left\{\frac{\Delta\omega}{\Omega^{(-)}}(1-\cos\Omega^{(-)}t)-i\sin\Omega^{(-)}t\right\}\times\hat{\phi}_{-1}^1(0)+\frac{1}{\Omega^{(-)2}}(\omega_1^2\cos\Omega^{(-)}t+\Delta\omega^2)\hat{\phi}_0^1(0)+\frac{\omega_1}{\sqrt{2}\Omega^{(-)}}\left\{\frac{\Delta\omega}{\Omega^{(-)}}(1-\cos\Omega^{(-)}t)+i\sin\Omega^{(-)}t\right\}\hat{\phi}_1^1(0). \tag{52}$$

This exact analytic solution is that obtained by replacing k,q by 1,0 in Eq. (48) of Ref. 11. The rest of the time evolution of the magnetization [i.e., $\phi_{\pm 1}^1(t)$] is obtained by substituting Eq. (52) into Eq. (34) and integrating. The solutions are again those obtained in Ref. 11.

Another case which can be treated to give closed-form solutions is that in which the kernel is degenerate of rank one[12]:

$$K(t,t')=A(t)B(t'), \tag{53}$$

where the functions $A(t)$ and $B(t)$ are linearly independent.

Expression (43) is then generalizable, giving

$$K^{n}(t,t')=\frac{A(t)B(t')}{(n-1)!}\left\{\int_{t'}^{t}A(x)B(x)dx\right\}^{n-1} \quad (54)$$

so that the resolvent kernel has the exact closed form:

$$\Gamma(t,t')=A(t)B(t')\exp\left\{\int_{t'}^{t}A(x)B(x)dx\right\}. \quad (55)$$

In general, however, the kernel is of a more complex nature. In the Bloch–Siegert problem, for instance, the modulated rf frequency has the form

$$\omega_{+1}(t)=\omega_1(e^{-i2\omega t}+1) \quad (56)$$

which upon substitution into Eq. (37) leads to the kernel

$$K(t,t')=\begin{cases}\left(\frac{\sin\Delta\omega t}{\Delta\omega}+\frac{\sin(\omega+\omega_0)t}{\omega+\omega_0}\right)[\cos\Delta\omega t'+\cos(\omega+\omega_0)t']+\left(\frac{\cos\Delta\omega t}{\Delta\omega}-\frac{\cos(\omega+\omega_0)t}{\omega+\omega_0}\right)\\ \times[\sin(\omega+\omega_0)t'-\sin\Delta\omega t']+\left(\frac{1}{\Delta\omega}-\frac{1}{\omega+\omega_0}\right)\sin 2\omega t', \quad \Delta\omega\neq 0\\ \left(t+\frac{\sin 2\omega_0 t}{2\omega_0}\right)(1+\cos 2\omega_0 t')-\frac{1+\cos 2\omega_0 t}{2\omega_0}\cdot\sin 2\omega_0 t'-t'(1+\cos 2\omega_0 t'), \quad \Delta\omega=0\end{cases} \quad (57)$$

which is degenerate of rank three. It can be shown[14] that the problem of solving a linear Volterra integral equation with kernel of rank n is reduced to solving an nth order linear ordinary differential equation. In fact, finding the solution to the integral equation for $\phi_0^1(t)$ in the Bloch–Siegert case can be reduced to solving a third order linear differential equation for which as noted by Bloch and Siegert,[2] a closed-form solution is virtually impossible to obtain. One can also see that obtaining a generalized expression for $K^n(t,t')$ using Eq. (57) can be a difficult, if not impossible, task. For many practical pulse shapes solving Eq. (35) exactly is also cumbersome. The utility of Eq. (35) depends upon finding a truncated form of the Neumann series solution. Attention must then be focused on the rapidity of the Neumann series convergence.

C. Series convergence

Given (i) that the kernel has upper bound M and continuous in a domain R: $a\leqslant t\leqslant b$ and $a\leqslant t'\leqslant b$ where $a,b\in\mathbb{R}$; (ii) that the inhomogeneous term is also bounded, $|\hat{\phi}_0^1(0)+W_{-1}(t)\hat{\phi}_1^1(0)+W_{+1}(t)\hat{\phi}_{-1}^1(0)|\leqslant N$ for some $N>0$ and $a\leqslant t\leqslant b$, then the nth term in the Neumann series solution, denoted by

$$\hat{\phi}_0^1(t)=\sum_{n=0}^{\infty}(-1)^nV_n(t), \quad (58)$$

obeys the inequality[13]

$$V_n(t)\leqslant\frac{N[(b-a)M]^n}{n!}. \quad (59)$$

For the Bloch–Siegert case, a gross estimate of the nth iterated integral term gives

$$V_n(t)\leqslant\begin{cases}\frac{\epsilon^n 10^n(\omega_0 t)^n}{n!}\left(\frac{\omega_0}{\Delta\omega}+\frac{\omega_0}{\omega+\omega_0}\right), & \omega\neq\pm\omega_0\\ \frac{\epsilon^n(\omega_0 t)^n 10^n}{n!}, & \Delta\omega=0\end{cases}, \quad (60)$$

where ϵ is the Bloch–Siegart shift (see Appendix B). Hence for a typical microsecond pulse with $\Delta\omega=0$ the error made in truncating the Neumann series to the first n terms has magnitude:

$$|\text{error}|\leqslant\frac{(10^{-2})^{n+1}}{2^{n+1}(n+1)!}. \quad (61)$$

The estimated error in truncating to include only $V_0(t)$ and $V_1(t)$is thus only 1.25×10^{-5} (i.e., 0.01% accuracy). For $\Delta\omega\neq0$, the series converges more rapidly as $\Delta\omega$ increases so that the solution of $\phi_0^1(t)$ is dominated by the first two terms in the Neumann series (38) for most practical situations. In fact, for any arbitrary pulse shape described by the field of Eq. (25) the kernel has the upper bound

$$K(t,t')\leqslant\begin{cases}\frac{2\gamma}{\Delta\omega}\{\sqrt{H_x^2(t')+H_y^2(t')}\}_{\max}, & \Delta\omega\neq0\\ 2\gamma\{\sqrt{H_x^2(t')+H_y^2(t')}\}_{\max}, & \Delta\omega=0\end{cases}, \quad (62)$$

where $\{f(t')\}_{\max}$ denotes the maximum value of a function f in $0\leqslant t'\leqslant t$ where t is the system evolution time. Using Eq. (59) the nth iterated integral has the bound

$$V_n(t)\leqslant\begin{cases}\frac{1}{n!}\left[\frac{2\gamma}{\Delta\omega}\{\sqrt{H_x^2(t')+H_y^2(t')}\}_{\max}t\right]^n, & \Delta\omega\neq0\\ \frac{1}{n!}\left[2\gamma\{\sqrt{H_x^2(t')+H_y^2(t')}\}_{\max}t\right]^n, & \Delta\omega=0\end{cases} \quad (63)$$

which shows that the Neumann series solution converges rapidly for $\gamma\{\sqrt{H_x^2+H_y^2}\}_{\max}t \cong 1$ (i.e., microsecond pulses for kilohertz rf frequencies) and increasingly rapid as $\Delta\omega$ is increased. This result parallels what is observed by Warren[8] when applying average Hamiltonian theory. Essentially the Magnus expansion is dominated by the first terms of the propagator for large $\Delta\omega$. The first two terms

$$V_0(t)=\hat{\phi}_0^1(0)+W_{+1}(t)\hat{\phi}_{-1}^1(0)+W_{-1}(t)\hat{\phi}_1^1(0) \tag{64}$$

and

$$V_1(t)=\int_0^t \mathrm{Re}\left\{\omega_1(t')e^{i\Delta\omega t'}\int_{t'}^t \omega_1^*(\bar{t})e^{-i\Delta\omega\bar{t}}\,d\bar{t}\right\} \times[\hat{\phi}_0^1(0)+W_{+1}(t')\hat{\phi}_{-1}^1(0) + W_{-1}(t')\hat{\phi}_1^1(0)]dt' \tag{65}$$

can hence be used as an accurate representation of the time evolution of the magnetization under any arbitrary well-behaved pulse shape using Eqs. (64) and (65) in Eq. (58) and the result in Eq. (34).

The first order term $V_0(t)$ involves the functions $W_{\pm 1}(t)$ which are essentially the Fourier transform of the pulse shape function $\omega_1(t)$ [assuming that $\omega_1(t')=0$ for $t'\leqslant 0$ and $t'\geqslant t$]. This result is in close connection to that obtained in Ref. 8 where it is found that the first approximation to the effective Hamiltonian is the Fourier transform of the pulse shape. Higher order terms [i.e., $V_1(t)$, $V_2(t)$, etc.] can also be related to higher order corrections to the effective Hamiltonian.

III. APPLICATIONS TO PUSLE SHAPE ANALYSIS

A. Exact solution for $\Delta\omega=0$ and rf fields for which $\omega_{+1}(t)=\omega_{-1}(t)$ [$\equiv\omega_1(t)$]

This roblem was previously discussed by the authors,[15] where the Hamiltonian (26) has $\omega=\omega_0$ ($\Delta\omega=0$) and $\omega_{+1}(t)=\omega_{-1}(t)$ which corresponds to a pulse with field components

$$H_x(t)=H_y(t)\equiv H'(t) \tag{66}$$

and

$$\omega_1(t)=\gamma H'(t). \tag{67}$$

The evolution equation (29) simplifies to

$$\dot{\hat{\phi}}_q^k(t)=\omega_1(t)\left[\frac{i}{2}\sqrt{(k+q)(k-q+1)}\hat{\phi}_{q-1}^k(t) + \frac{i}{2}\sqrt{(k-q)(k+q+1)}\hat{\phi}_{q+1}^k(t)\right]. \tag{68}$$

By defining a set of functions

$$f_q^k[\beta(t)]=\hat{\phi}_q^k(t), \tag{69}$$

where the new variable β is given by

$$\beta(t)=\int_0^t \omega_1(t')dt', \tag{70}$$

Eq. (68) takes on the form of Eq. (42) of Ref. 11:

$$\frac{d}{d\beta}f_q^k(\beta)=\frac{i}{2}\sqrt{(k+q)(k-q+1)}f_{q-1}^k(\beta) + \frac{i}{2}\sqrt{(k-q)(k+q+1)}f_{q+1}^k(\beta). \tag{71}$$

This corresponds to the case in which the integral equation for the magnetization in the new variable β is given by

$$f_0^1(\beta)=f_0^1(0)+\frac{i}{\sqrt{2}}\beta[f_1^1(0)+f_{-1}^1(0)] - \int_0^\beta(\beta-\beta')f_0^1(\beta')d\beta', \tag{72}$$

where the kernel is evidently a function of $(\beta-\beta')$. The magnetization is then exactly soluble by invoking the Laplace–Faltung theorem to Eq. (72).

This set of equations is also solved exactly by employing the transformation of Eq. (43) in Ref. 11 with $\theta=\pi/2$ giving the solution after transforming back to the laboratory frame:

$$\phi_q^k(t)=e^{iq(\omega_0 t-\phi)}\sum_{\bar{q}q'}\exp\left\{i\bar{q}\int_0^t\omega_1(t')dt'\right\} \times d_{\bar{q}q}^{(k)}\left(\frac{\pi}{2}\right)d_{\bar{q}q'}^{(k)}\left(\frac{\pi}{2}\right)\phi_{q'}^k(0). \tag{73}$$

Using the group property of the Wigner rotation matrices,[16] the solution is recast in the form of a Wigner rotation:

$$\phi_q^k(t)=e^{iq\omega_0 t}\sum_{q'}\mathscr{D}_{qq'}^{(k)}\left[\phi-\frac{\pi}{2},\beta(t),\frac{\pi}{2}-\phi\right]\phi_{q'}^k(0), \tag{74}$$

where $\beta(t)$ depends upon the pulse shape $\omega_1(t)$. The exact analytical solution (73) or (74) to the spin density matrix then provides a description of any resonant pulse shape that fits the general condition (66).

B. $\sin(\omega_c t)/t$ pulse envelopes

Consider the cases now when condition (66) is not imposed and off-resonance effects are allowed. The magnetic field in the pulse experiment is assumed to have an rf field modulation of the sinc form with rf field components:

$$H_x(t)=\frac{\sin(\omega_c t)}{t}\cos\omega t \tag{75}$$

and

$$H_y(t)=\frac{\sin(\omega_c t)}{t}\sin\omega t. \tag{76}$$

Using the integral equations approach, the solutions to the NMR observables after 90° and 180° pulses are given by the first order approximation [i.e., $V_0(t)-V_1(t)$] to the perturbation expansion developed in Sec. II B. Hence, integrating Eq. (65) numerically to within 1% accuracy, the behavior of $\phi_0^1(t)$ and, therefore, population changes are given. We here discuss only population changes (starting from equilibrium); other observables such as in- and out-of-phase polarizations are easily obtainable from Eqs. (34) and (65). The results are given in Figs. 1 and 2.

As observed in the curves of Fig. 1, excitation sidebands

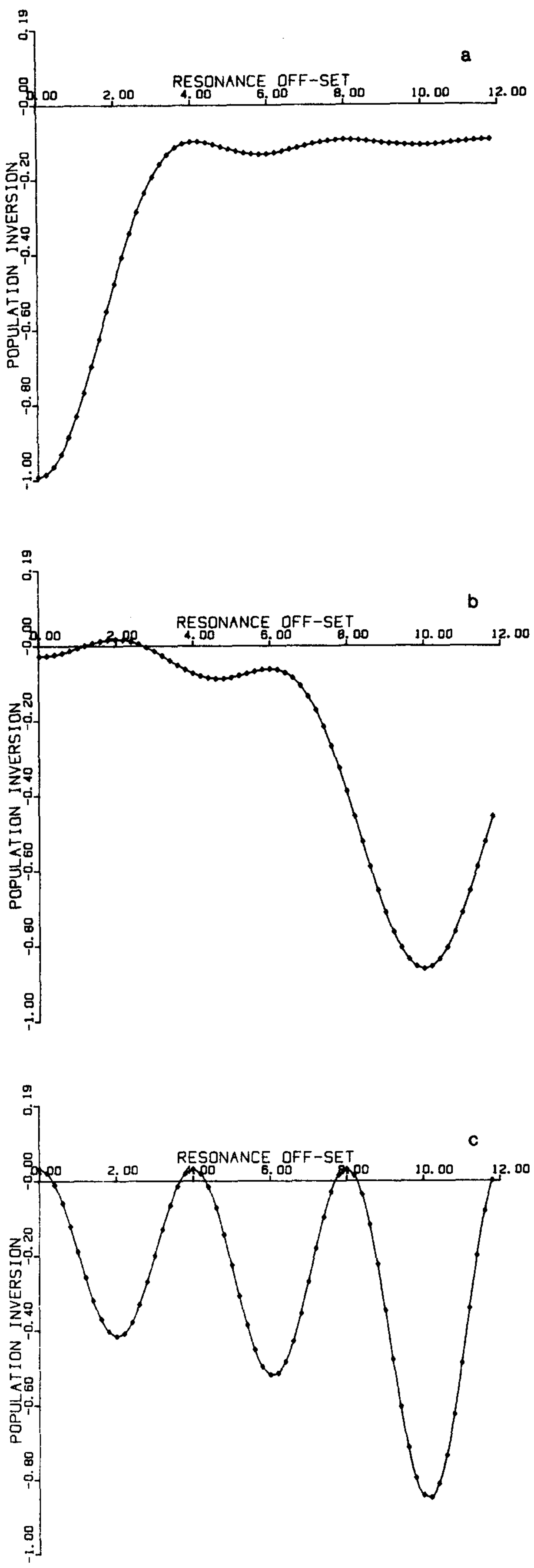

FIG. 1. Population changes (inversions) for 90° sinc pulse with carrier frequencies (a) $\omega_c = \omega_1$; (b) $\omega_c = 10\omega_1$; and (c) $\omega_c = 100\omega_1$.

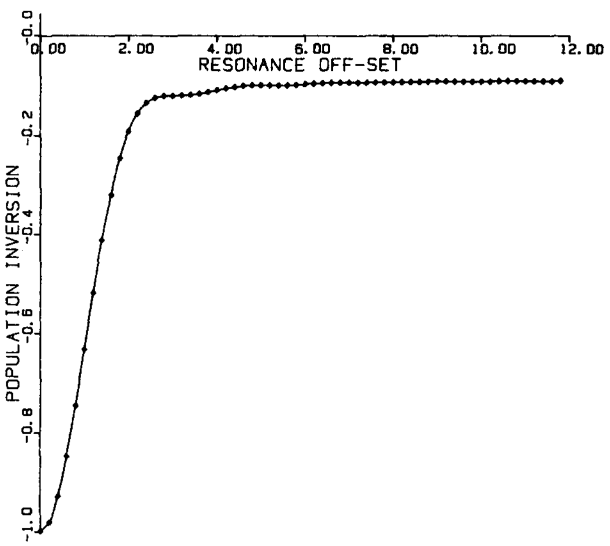

FIG. 2. Population change (inversion) for a 180° sinc pulse with carrier frequency $\omega_c = \omega_1$.

for 90° pulses appear far from resonance as is known.[8,17] An interesting feature, however, is that the inversion is rather selective and can be controlled by monitoring the carrier frequency ω_c of the pulse envelope. For a carrier frequency equal to the rf frequency ω_1 a selective inversion occurs about $\Delta\omega = 0$; for $\omega_c = 10\omega_1$ inversion is less selective and peaks about $\Delta\omega = 10\omega_1$; and for $\omega_c = 100\omega_1$ the inversion pattern is rather nonselective. In contrast, in a 180° pulse inversion tends to be more uniform with a large peak at $\Delta\omega = 0$ for carrier frequency $\omega_c = \omega_1$ (see Fig. 2). This poses an advantage for $\sin(\omega_c t)/t$ envelopes over pure rectangular pulses, where the achievement of such a selective excitation of the spins relies on the ability to create appropriate composite pulse sequences.[18]

C. Gaussian pulse envelopes

A simple way of eliminating significant excitation sidebands (inversions far from resonance) which arise when pulsing with rectangular pure pulses, for instance, is to use a Gaussian pulse whose shape is depicted by

$$\omega_1(t) = \omega_1 \exp[-(t/\tau)^2]. \tag{77}$$

The field components are given by

$$H_x(t) = \omega_1 \exp[-(t/\tau)^2]\cos \omega t \tag{78}$$

and

$$H_y(t) = \omega_1 \exp[-(t/\tau)^2]\sin \omega t. \tag{79}$$

By using the first order perturbation solution (65), numerical integration gives a population inversion (for a 90° pulse) given by Fig. 3. The value for the parameter τ is chosen to be $1/\omega_1$. This, as shown, produces a desirable localized inversion about $\Delta\omega = 0$ without high frequency sidebands. By increasing the parameter τ (i.e., decreasing the width of the Gaussian pulse) to orders of magnitude greater than $1/\omega_1$, sidebands are created causing inversions far from resonance. By employing a Gaussian pulse envelope, of appropriate width, it is therefore possible to avoid the problem of inver-

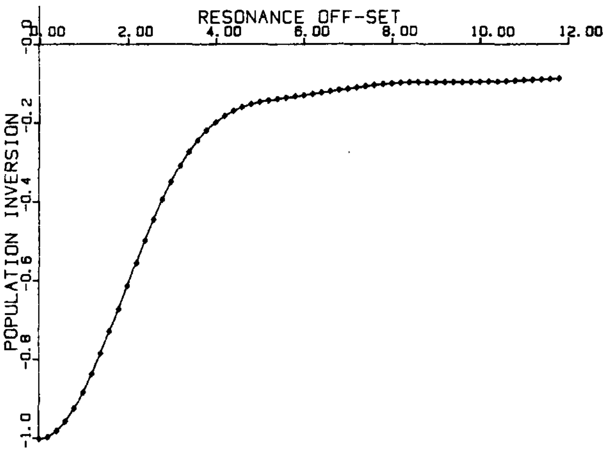

FIG. 3. Uniform population inversion for a 90° Gaussian pulse with pulse shape $\omega_1(t) = \omega_1 \exp[(-t/\tau)^2]$, where τ is chosen to be $1/\omega_1$.

sion sidebands which is common to rectangular or $\sin(\omega_c t)/t$ pulses. For more uniform inversions, it is preferable to use a pulse shape which decays quickly in the time domain (microsecond times). Gaussian pulse shapes can satisfy this criterion, but even more localized inversions can be produced by crafting pulses which have a form of a polynomial times a Gaussian (i.e., Hermite pulse envelopes).[8] These pulse shapes can be understood by the same approach used for the Gaussian and $\sin(\omega_c t)/t$ pulses. Such pulses have already been rationalized by coherent averaging methods.[8]

APPENDIX A

Most useful properties of the $\mathcal{Y}^{(k)q}(\mathbf{I})$[10]:

(i) Expansion in the $|IM\rangle\langle IM'|$ basis (reduced matrix element)

$$\mathcal{Y}^{(k)q}(\mathbf{I}) = (i)^k[(2I+1)(2k+1)]^{1/2} \sum_{MM'} (-1)^{I-M} \times \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} |IM\rangle\langle IM'| \quad \text{(A1)}$$

whose inverse gives

$$|IM\rangle\langle IM'| = (2I+1)^{-1/2}(-1)^{I-M} \sum_{kq} (2k+1)^{1/2}(-i)^k \times \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} \mathcal{Y}^{(k)q}(\mathbf{I}). \quad \text{(A2)}$$

(ii) Operator adjoint

$$\mathcal{Y}^{(k)q\dagger}(\mathbf{I}) = (-1)^{k-q}\mathcal{Y}^{(k)-q}(\mathbf{I}) \equiv \mathcal{Y}_q^{(k)}(\mathbf{I}). \quad \text{(A3)}$$

(iii) Matrix elements (Wigner–Eckart theorem)

$$\langle\langle \mathcal{Y}^{(k)q} | \mathcal{Y}^{(L)m} | \mathcal{Y}^{(k')q'} \rangle\rangle = \mathrm{Tr}\{\mathcal{Y}^{(k)q\dagger}\mathcal{Y}^{(L)m}\mathcal{Y}^{(k')q'}\} = (-1)^{2I+L-k'+q}(i)^{k'+L+k} \times [(2L+1)(2k+1)(2k'+1)]^{1/2} \times (2I+1)^{3/2} \begin{pmatrix} k & L & k' \\ -q & m & q' \end{pmatrix} \begin{Bmatrix} I & I & k' \\ L & k & I \end{Bmatrix}, \quad \text{(A4)}$$

where

$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$ is a 3-j and $\begin{Bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{Bmatrix}$ is a 6-j coefficient.[16]

(iv) Commutation relation[10]

$$[\mathcal{Y}^{(L)m}(\mathbf{I}), \mathcal{Y}^{(k)q}(\mathbf{I})]_- = \frac{2}{2I+1} \sum_{k'q'} \phi(kLk') \times \langle\langle \mathcal{Y}^{(k')q'}(\mathbf{I}) | \mathcal{Y}^{(L)m}(\mathbf{I}) | \mathcal{Y}^{(k)q}(\mathbf{I}) \rangle\rangle \times \mathcal{Y}^{(k')q'}(\mathbf{I}), \quad \text{(A5)}$$

where $\phi(L_1L_2L_3) = 1$ for $L_1 + L_2 + L_3$ odd and zero otherwise.

APPENDIX B

In this Appendix, it is shown how the Bloch–Siegert problem can be treated by a systematic rotating frame approach in Liouville space (decomposed in the spherical tensor basis).

We consider a field with both rotating and counterrotating components oscillating at frequency ω:

$$\mathbf{H}(t) = 2H_1 \cos \omega t \hat{x} + H_0 \hat{z}. \quad \text{(B1)}$$

Assuming a Zeeman interaction, the density matrix in the laboratory axis evolves as [cf. Eq. (29)]

$$\dot{\phi}_q^k(t) = iq\omega_0\phi_q^k(t) + \frac{i\omega_1}{2}(e^{i\omega t} + e^{-i\omega t}) \times \sqrt{(k+q)(k-q+1)}\phi_{q-1}^k(t) + \frac{i\omega_1}{2}(e^{i\omega t} + e^{-i\omega t}) \times \sqrt{(k-q)(k+q+1)}\phi_{q+1}^k(t). \quad \text{(B2)}$$

Equation (B2) is now solved by a succession of transformations which eliminate the time dependence to within a given approximation. In the integral equation approach, such transformations correspond to approximating the kernel $K(t,t')$ as an effective function of $(t-t')$.

1. Zeroth and first order approximations

$$\hat{\phi}_q^k(t) = \exp(iq\omega t)\phi_q^k(t) \quad \text{(B3)}$$

renders the counterrotating field component static giving

$$\dot{\hat{\phi}}_q^k(t) = iq(\omega_0 + \omega)\hat{\phi}_q^k(t) + \frac{i\omega_1}{\sqrt{2}} \times \sqrt{(k+q)(k-q+1)}\hat{\phi}_{q-1}^k(t) + \frac{i\omega_1}{\sqrt{2}}\sqrt{(k-q)(k+q+1)}\hat{\phi}_{q+1}^k(t) + \frac{i\omega_1}{2}e^{i2\omega t}\sqrt{(k+q)(k-q+1)}\hat{\phi}_{q-1}^k(t) + \frac{i\omega_1}{2}e^{-i2\omega t}\sqrt{(k-q)(k+q+1)}\hat{\phi}_{q+1}^k(t). \quad \text{(B4)}$$

The zeroth order solution is obtained by assuming the harmonic terms of frequencies $\pm 2\omega$ to average to zero. The solution then corresponds to the case of a pure rectangular pulse. To first order, however, the counterrotating field of amplitude ω and now frequency 2ω has a component perpendicular to the z axis which will drive a resonance given by

$$2\omega = \sqrt{(\omega_0+\omega)^2+\omega_1^2}$$

or

$$\omega \approx \omega_0(1+\epsilon/2), \tag{B5}$$

where $\epsilon = \omega_1^2/2\omega_0^2$ is the Bloch–Siegert shift.

Hence Eq. (B5) gives the resonance frequency to first order in ϵ. Equation (B4) is then diagonalized to the θ' axis.

2. Second order approximations

The transformation which diagonalizes Eq. (B4) within a factor of ϵ^2 is

$$\bar{\psi}_{\bar{q}}^k(t) = \sum_{qq'} d_{\bar{q}q}^{(k)}(\xi) e^{-iq2\omega t} d_{qq'}^{(k)}(\theta') e^{iq'\omega t} \phi_{q'}^k(t) \tag{B6}$$

with

$$\tan\theta' = \frac{\omega_1}{\omega_0+\omega}, \tag{B7}$$

$$\tan\xi = \frac{\omega_1^{(+)}}{\Omega^{(+)}-2\omega}, \tag{B8}$$

$$\Omega^{(+)} = \sqrt{(\omega_0+\omega)^2+\omega_1^2}, \tag{B9}$$

and

$$\omega_1^{(+)} = \tfrac{1}{2}\omega_1(1+\cos\theta'). \tag{B10}$$

The density matrix equation then reads

$$\dot{\bar{\psi}}_{\bar{q}}^k(t) = i\bar{q}\Omega^{(+)'}\bar{\psi}_{\bar{q}}^k(t), \tag{B11}$$

where

$$\Omega^{(+)'} = \sqrt{(\Omega^{(+)}-2\omega)^2+\omega_1^{(+)2}}. \tag{B12}$$

Solving Eq. (B11) and transforming back to the laboratory frame using the inverse of Eq. (B6) the density matrix has the solution

$$\phi_q^k(t) = e^{-iq\omega t} \sum_{q''\bar{q}} \sum_{\bar{q}'} e^{i\bar{q}'2\omega t} d_{\bar{q}\bar{q}'}^{(k)}(\xi) d_{\bar{q}'q}^{(k)}(\theta') e^{i\bar{q}\Omega^{(+)'}t}$$
$$\times \sum_{q'} d_{\bar{q}q'}^{(k)}(\xi) d_{q'q''}^{(k)}(\theta') \phi_{q''}^k(0) \tag{B13}$$

correct to second order in ϵ.

The resonance frequency corresponds to the minimum value of the static field in the final transformed frame,[19] hence differentiating

$$\frac{\partial\Omega^{(+)'2}}{\partial\omega_0} = 0$$

or

$$\omega = \omega_0 + \frac{\omega\omega_1^2}{(\omega_0+\omega)^2} + \frac{(2\omega_0-\omega)\omega_1^4}{4(\omega_0+\omega)^4} + \cdots, \tag{B14}$$

so

$$\omega \cong \omega_0\left(1+\frac{\epsilon}{2}+\frac{\epsilon^2}{16}\right) \tag{B15}$$

is the resonance frequency to second order.

3. Third order approximations

To diagonalize Eq. (B4) within a factor of ϵ^3, we employ the frequency-modulated transformation

$$\bar{\psi}_{\bar{q}}^k(t) = \sum_{qq'} d_{\bar{q}q}^{(k)}(\lambda) \exp\left\{-iq\frac{\omega_1}{2}\sin\theta'\sin 2\omega t\right\}$$
$$\times e^{-iq2\omega t} e^{iq'\omega t} d_{qq'}^{(k)}(\theta')\phi_{q'}^k(t), \tag{B16}$$

leading to the solution

$$\bar{\psi}_{\bar{q}}^k(t) = \exp(i\bar{q}\Omega^{(+)''}t)\bar{\psi}_{\bar{q}}^k(0) \tag{B17}$$

with

$$\tan\lambda = \frac{\omega_1^{(+)}J_0(\omega_1\sin\theta'/2\omega)}{\Omega^{(+)}-2\omega} \tag{B18}$$

and

$$\Omega^{(+)''} = \sqrt{(\Omega^{(+)}-2\omega)^2 + [\omega_1^{(+)}J_0(\omega_1\sin\theta'/2\omega)]^2}. \tag{B19}$$

The $J_n(\chi)$ term is a Bessel function of nth order. Using the inverse of Eq. (B16), the density matrix in the laboratory frame has the solution

$$\phi_q^k(t) = e^{-iq\omega t} \sum_{q''\bar{q}\bar{q}'} \exp\left\{\frac{\omega_1}{2\omega}\sin\theta'\sin 2\omega t + 2\omega t\right\}$$
$$\times e^{i\bar{q}\Omega^{(+)''}t} d_{q''q}^{(k)}(\theta') d_{\bar{q}q''}^{(k)}(\lambda)$$
$$\times d_{\bar{q}\bar{q}}^{(k)}(\lambda) d_{\bar{q}q'}^{(k)}(\theta')\phi_{q'}^k(0). \tag{B20}$$

The resonance frequency to third order in ϵ is given by the minimum in $\Omega^{(+)''2}$:

$$\Omega^{(+)''2} = (\omega_0-\omega)^2 + 2\omega\frac{\omega_1^2}{\omega_0+\omega} - \frac{\omega_0\omega_1^4}{2(\omega_0+\omega)^3}$$
$$-\frac{(\omega_0+\omega)^3+2\omega^3}{8\omega^2(\omega_0+\omega)^5}\omega_1^6 + \cdots, \tag{B21}$$

so

$$\omega \cong \omega_0\left(1+\frac{\epsilon}{2}+\frac{5}{16}\epsilon^2+\frac{13}{64}\epsilon^3\right). \tag{B22}$$

Except for the third order frequency (B22), where we have neglected the $\omega_1^{(+)}J_{\pm 1}(\chi)$ and $\omega_1^{(-)}J_0(\chi)$ terms which give rise to slight corrections in the coefficient of ω_1^6 in Eq. (B21), the results of this Appendix duplicate exactly those of Pegg[20,21]; Hannaford, Pegg, and Series[22]; where only the resonance frequency shifts were calculated.

APPENDIX C

Here it is shown how the method of transformations (using spherical tensor theory) can be used to formulate steady-state magnetic resonance experiments. We treat the problem of an ensemble of nuclei with spin density matrix $\sigma(t)$ characterized with magnetic moment $\mu = \hbar\gamma\mathbf{I}$, interacting with a rotating field while subject to an isotropic random process of relaxation and some pumping process which depletes and populates some particular eigenstates of I_z.[19] An optical pumping experiment, for instance, in which broadband light causes some states to populate and by radiative decay relaxes the system, leads to such a treatment.

The complete quantum Liouville equation of motion which describes the evolution of the ensemble including the relaxation and regeneration processes is

$$\dot{\sigma}(t) = -i[\mathscr{H}_1(t),\sigma(t)]_- - \hat{\Gamma}\sigma(t) + \sum_{n,n'} R_{nn'}(t)\xi_{nn'}. \tag{C1}$$

The term $-\hat{\Gamma}\sigma$ describes relaxation where Γ is, in general, a relaxation superoperator. The term $\Sigma_{n,n'}R_{nn'}(t)\xi_{nn'}$ ($\equiv \Sigma_{n,n'}R_{nn'}(t)|In\rangle\langle In'|$) represents a linear combination of all possible regenerations into the $|In\rangle$ states from the $|In'\rangle$ states at rates given by the coefficients $R_{nn'}(t)$ which, in general, may depend on time.

The solution of Eq. (C1) is obtained by using the multipole expansion (17) of $\sigma(t)$ giving

$$\dot{\phi}^k_q = \sum_{k'q'} \left\langle\left\langle \mathscr{Y}^{(k)q}\left|\left[\frac{-i}{\hbar}\mathscr{H}_1(t),\mathscr{Y}^{(k')q'}\right]_-\right.\right\rangle\right\rangle \phi^{k'}_{q'} - \Gamma^k_q\phi^k_q + \sum_{nn'} R_{nn'}(t)\langle\langle \mathscr{Y}^{(k)q}|\xi_{nn'}\rangle\rangle, \tag{C2}$$

where

$$\langle\langle \mathscr{Y}^{(k)q}|\hat{\Gamma}|\mathscr{Y}^{(k')q'}\rangle\rangle = \delta_{kk'}\delta_{qq'}\Gamma^k_q \tag{C3}$$

(Γ^k_q a constant) so that the relaxation superoperator is diagonal in the spherical tensor basis.

Transforming to a frame defined by

$$\hat{\psi}^k_{\bar{q}}(t) = \sum_q d^{(k)}_{\bar{q}q}(\theta)e^{(\Gamma^k_q - iq\omega)t}\phi^k_q(t) \tag{C4}$$

with

$$\tan\theta = \frac{\omega_1}{\omega_0 - \omega}, \tag{C5}$$

Eq. (C2) is put to diagonal form:

$$\dot{\hat{\psi}}^k_{\bar{q}}(t) = i\bar{q}\Omega^{(-)}\hat{\psi}^k_{\bar{q}}(t) + \sum_{qnn'} d^{(k)}_{\bar{q}q}(\theta) \times e^{(\Gamma^k_q - iq\omega)t}R_{nn'}(t)\langle\langle \mathscr{Y}^{(k)q}|\xi_{nn'}\rangle\rangle \tag{C6}$$

whose formal solution is (in the laboratory frame)

$$\phi^k_q(t) = e^{-\Gamma^k_q t}e^{iq\omega t}\sum_{\bar{q}q'} d^{(k)}_{\bar{q}q}(\theta)e^{i\bar{q}\Omega^{(-)}t}d^{(k)}_{\bar{q}q'}(\theta)\phi^k_{q'}(0) + \sum_{\bar{q}q'\bar{n}n'} d^{(k)}_{\bar{q}q}(\theta)e^{i\bar{q}\Omega^{(-)}t}d^{(k)}_{\bar{q}q'}(\theta)\langle\langle \mathscr{Y}^{(k)q'}|\xi_{\bar{n}n'}\rangle\rangle \times \int_0^t R_{\bar{n}n'}(t')e^{-i(\bar{q}\Omega^{(-)}+q'\omega)t'}e^{-\Gamma^k_q(t-t')}dt', \tag{C7}$$

where

$$\Omega^{(-)} \equiv \sqrt{\Delta\omega^2 + \omega_1^2}. \tag{C8}$$

The first term in this solution damps out in a time $t \gg \Gamma^{k\,-1}_q$ so that only the second term gives the steady-state solution. The system, in the steady state, then evolves independently of the initial state preparations $\phi^k_q(0)$.

A noteworthy feature of the steady-state solution lies in the regeneration or pumping mechanism which is described by the matrix elements $R_{\bar{n}n'}(t)$. The outcome of the NMR experiment may be controlled by monitoring the $R_{\bar{n}n'}(t)$ coefficients. This then leads to interesting physical and experimental consequences, some of which are considered here:

We first rewrite the steady-state solution of Eq. (C7) by evaluating the trace using Eq. (A1), $\langle\langle \mathscr{Y}^{(k)q'}|\xi_{\bar{n}n'}\rangle\rangle = \langle In'|\mathscr{Y}^{(k)q'\dagger}|I\bar{n}\rangle$

$$= \langle I\bar{n}|\mathscr{Y}^{(k)q'}|In'\rangle^* = (-i)^k\sqrt{(2I+1)(2k+1)}(-1)^{I-\bar{n}} \times \begin{pmatrix} I & k & I \\ -\bar{n} & q' & n \end{pmatrix}. \tag{C9}$$

The steady-state solution, in general, is then given by

$$\phi^k_q(t) = e^{iq\omega t}\sum_{\bar{q}q'm} e^{iq\Omega^{(-)}t}d^{(k)}_{\bar{q}q'}(\theta)d^{(k)}_{\bar{q}q}(\theta)(-i)^k \times\sqrt{(2I+1)(2k+1)}(-1)^{I-m} \times \begin{pmatrix} I & k & I \\ -m & q' & m-q' \end{pmatrix}\int_0^t R_{m,m-q'}(t') \times e^{-i(\bar{q}\Omega^{(-)}+q'\omega)t'}e^{-\Gamma^k_q(t-t')}dt'. \tag{C10}$$

(i) For time-independent excitations the integral in Eq. (C10) is evaluated immediately giving

$$\phi^k_q(t) = (-i)^k\sqrt{(2I+1)(2k+1)} \times\sum_{\bar{q}\bar{n}n'}(-1)^{I-\bar{n}}d^{(k)}_{\bar{q},\bar{n}-n'}(\theta)\,d^{(k)}_{\bar{q}q}(\theta)R_{\bar{n}n'} \times \begin{pmatrix} I & k & I \\ -\bar{n} & \bar{n}-n' & n' \end{pmatrix} \times\frac{e^{i(q+n'-\bar{n})\omega t}}{\Gamma^k_q - i[\bar{q}\Omega^{(-)} + (\bar{n}-n')\omega]} \tag{C11}$$

as the steady-state solution of the density matrix. We observe that for a preferential pumping to an eigenstate $|In\rangle$ from a state $|In+q\rangle$ (i.e., $R_{\bar{n}n'} = R_{n+q,n}\delta_{\bar{n},n+q})\delta_{nn'}$ the time dependence of the qth quantum coherences, ϕ^k_q for $k = 0,1,...,2I$, is eliminated. A special case of this is a mechanism which pumps into a specific state $|In\rangle$ preferentially (i.e., $R_{\bar{n}n'} = R\delta_{\bar{n}n}\delta_{n'n}$) so that all zero quantum coherences ϕ^k_0 are time independent. From the expansion (A2) we conclude that the diagonal elements of the spin density matrix in the $|IM\rangle\langle IM'|$ basis do not evolve in time. In other words, the energy level populations stay constant in time; a result noted by Series.[19] Also to be remarked is that the denominators in Eq. (C11) pass through minimum values for $\Omega^{(-)}$ a minimum (i.e., for $\omega = \omega_0$). As a result the signals are at maximum amplitudes at resonance. For polarizations $\phi^k_{q'}$ with $q' \neq n - n'$ the time dependence is a modulation at harmonics of the driving frequency ω.

(ii) In time-modulated excitations we consider the Fourier decomposition of the regeneration coefficients

$$R_{\bar{n}n'}(t) = \sum_{n=-\infty}^{+\infty} a^n_{\bar{n}n'}e^{i\nu nt}, \tag{C12}$$

where $a^n_{\bar{n}n'}$ are the Fourier components. In the steady-state limit, the polarizations now evolve as

$$\phi_q^k(t) = (-i)^k\sqrt{(2I+1)(2k+1)} \times \sum_{\bar{q}\bar{n}nn'} d^{(k)}_{\bar{q},\bar{n}-n'}(\theta) d^{(k)}_{\bar{q}q}(\theta)(-1)^{I-\bar{n}} \times \begin{pmatrix} I & k & I \\ -\bar{n} & \bar{n}-n' & n' \end{pmatrix} a^n_{\bar{n}n'} \times \frac{e^{i[n\nu+(q+n'-\bar{n})\omega]t}}{\Gamma_q^k + i[n\nu - \bar{q}\Omega^{(-)} + (n'-\bar{n})\omega]}. \quad \text{(C13)}$$

The denominators in Eq. (C13) now pass through minimum values at

$$\bar{q}\Omega^{(-)} + (\bar{n}-n')\omega = n\nu, \quad \text{(C14)}$$

therefore altering the resonance condition from the case of time-independent pumping where the observables are maximized at the Larmor frequency ω_0.

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