ELSEVIER

8 November 1996

Chemical Physics Letters 262 (1996) 17–26

CHEMICAL PHYSICS LETTERS

A theoretical approach to the analysis of arbitrary pulses in magnetic resonance

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Received 24 July 1996; in final form 9 September 1996

Abstract

We introduce split Hamiltonian theory (SHT) to analyze arbitrary pulses in magnetic resonance, i.e. pulses substantial in magnitude but not non-selective. The range of validity of the lower order approximations is discussed, and the method is illustrated by applying it to the consideration of pulse adjustable spectroscopies in time domain ESR that are utilized to study nuclear modulation. A virtue of SHT is that, whereas the approximate analytic solutions can provide useful insights, it can also be iterated numerically to achieve quantitatively accurate solutions.

1. Introduction

Sophisticated pulse sequences in magnetic resonance are usually conveniently treated as involving either (i) non-selective pulses and/or (ii) highly-selective pulses depending upon whether the intensity of the irradiating field is in the limit of (i) $\boldsymbol{H}_1 \gg |\boldsymbol{H}_0|$ (where $\boldsymbol{H}_1$ is the term in the spin Hamiltonian representing the interaction of the spin with the radiation field, and $\boldsymbol{H}_0$ is the spin Hamiltonian responsible for the free evolution of the spins in the absence of the radiation), or (ii) $|\boldsymbol{H}_1| \ll |\boldsymbol{H}_0|$. (Herein, we take $\boldsymbol{H}_0$ and $\boldsymbol{H}_1$ to be the rotating-frame forms.) There are many cases in magnetic resonance, especially in ESR where $|\boldsymbol{H}_1| \lesssim |\boldsymbol{H}_0|$ (referred to herein as "arbitrary pulses"), and this poses difficulties in the analysis of such pulse sequences, short of detailed numerical computations [1]. Thus, for example, in ESR we have pulse adjustable spectroscopies based on the "2 + 1" and "1 + 2" pulse sequences [2–4] which enhance sensitivity to nuclear modulation, and deviations from case (i) are needed to generate observable double quantum coherences [5]. Also, in NMR deviations from case (i) can be used to generate multiple quantum spin-echoes from just two pulses (see Ref. [6], p. 245; see also Ref. [7]). In these cases detailed numerical computations have been used to analyze the experiments, but they do not provide the convenient predictive power that an analytic theory offers. Tsvetkov and co-workers [8] and Schweiger and co-workers [9–12] have addressed this by approximate analytic approaches for studies of nuclear modulation in the case of $|\boldsymbol{H}_1| \ll |\boldsymbol{H}_0|$ and/or selective excitation.

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PII S0009-2014(96)01044-5

Some time ago Zientara and Freed [13] succeeded in dealing numerically with the time evolution of nuclear spins governed by a stochastic Liouville equation (SLE) in what they called the ''double-step'' procedure. In this procedure, the density matrix solution $\rho(t) = \exp(-i\Omega t + Wt)\rho(0)$ is approximated by a series of n steps in time $\Delta t = t/n$ short enough that $\exp(-i\Omega\Delta t + W\Delta t) \approx \exp(i\Omega\Delta t)\exp(W\Delta t)$, which leads to a convenient numerical solution, since the well-defined properties of the ''frequency-matrix'' Ω and the ''jump matrix'' W, could be treated separately without the complications (due to $[\Omega, W] \neq 0$) of treating their combined effects. More recently, Liang and Freed [14] have utilized such a ''double-step'' procedure in numerical analyses of the effects of imperfect pulses in slow-motional 2D-FT-ESR using the SLE. They found that an $n = 8$ would accurately represent a $\pi/2$ pulse with $|\boldsymbol{H}_1| \lesssim |\boldsymbol{H}_0|$. Also Usova et al. [15] have used such an approach to introduce the effects of molecular dynamics trajectories into the time evolution of the spin density matrix.

Given the rapid numerical convergence of this approach, it appeared reasonable to attempt approximate analytic solutions by the ''double-step'' procedure for pulse sequences in the absence of relaxation, which involve one or more ''arbitrary pulses''. Of particular importance is the existence of a convergence theorem for such a procedure. This is given by the Trotter formula [16]:

$$\lim_{n\to\infty} [\exp(\boldsymbol{A}/n)\exp(\boldsymbol{B}/n)]^n = \exp(\boldsymbol{A}+\boldsymbol{B}), \tag{1}$$

for bounded operators $\boldsymbol{A}$ and $\boldsymbol{B}$. For finite values of n, Suzuki has obtained error estimates [17]. In modified or ''symmetrized form'' one has:

$$\exp(\boldsymbol{A}+\boldsymbol{B}) \approx [\exp(\boldsymbol{A}/2n)\exp(\boldsymbol{B}/n)\exp(\boldsymbol{A}/2n)]^n, \tag{2}$$

with the approximant on the rhs converging to the lhs as n^{-2} with increasing n [17]. (More precise convergence criteria are given in Ref. [17].) Thus, such a method should converge rapidly if e.g. $\boldsymbol{A} = \boldsymbol{H}_0 t_p$ and $\boldsymbol{B} = \boldsymbol{H}_1 t_p$, and t_p is such that $|\boldsymbol{H}_1 t_p| \approx \pi/2$, or π, etc.

In this Letter we introduce a method based upon Eq. (2) to provide analytical estimates of the effects of arbitrary pulses in magnetic resonance. That is, we write for the propagator $\boldsymbol{R}$:

$$\boldsymbol{R} \equiv \exp[-i(\boldsymbol{H}_0 + \boldsymbol{H}_1)t_p] \tag{3}$$

the nth order approximation:

$$\boldsymbol{R}_n \approx (\tilde{\boldsymbol{R}}(n))^n \tag{4a}$$

in terms of the nth symmetrized double step:

$$\tilde{\boldsymbol{R}}(n) = \exp(i\boldsymbol{H}_0 t_p/2n)\exp(-i\boldsymbol{H}_1 t_p/n)\exp(-i\boldsymbol{H}_0 t_p/2n). \tag{4b}$$

We shall refer to the method of Eqs. (4) as ''split Hamiltonian theory''. The practical advantage of using Eq. (4) in this fashion for analytical purposes is that the arbitrary pulse is replaced by a simple sequence of non-selective pulses with rotation angles of $\pi/2n$ or π/n etc., alternating with the free evolution of the spins. Then standard methods, such as the product operator approach, utilized to analyze pulse sequences with non-selective pulses [18], can be employed to analyze each arbitrary pulse in the actual pulse sequence. [2] This is practical provided reasonable approximations are obtained from small n. That is, for small n, one should obtain manageable expressions yielding a semi-quantitative description of the effects of the pulse sequence. When full quantitative accuracy is desired, it is always possible to use a large enough n to guarantee convergence in numerical computations. We shall develop useful convergence criteria for an arbitrary pulse in the next section, which are checked by numerical computations.

[2] It is, perhaps of some interest to note that the DANTE pulse sequence in NMR [19] is an attempt to produce the equivalent of a selective pulse by a sequence of small-flip-angle non-selective pulses. This is, of course, different from the objective of the present work of using non-selective pulses in theoretical calculations of arbitrary pulses.

In the Letter we provide an assessment of this approach to arbitrary pulses. We show that with n as small as 2 or 4, semi-quantitative results are obtained. We then use this split Hamiltonian method to develop useful expressions to describe some pulse sequences of current interest which contain adjustable (or arbitrary) pulses.

2. Model system

We now examine the split Hamiltonian approximation by applying it to a simple case for which the analytic solution is known. We consider the model system of a single spin of $S = 1/2$ in an external constant magnetic field B_0 along the z-axis and a circularly polarized radiation field B_1 along the rotating x-axis. The spin Hamiltonian of this system in the rotating frame (in angular frequency units) is:

$$\boldsymbol{H} = \Delta\omega \boldsymbol{S}_z + \omega_1 \boldsymbol{S}_x, \tag{5}$$

where $\Delta\omega = \omega_0 - \omega$ and $\omega_0 = \gamma B_0$ with $\omega_1 = \gamma B_1$. During a pulse, the propagator, $\boldsymbol{R}$ is given by

$$\boldsymbol{R} = \exp\left[-\mathrm{i}(\Delta\omega \boldsymbol{S}_z + \omega_1 \boldsymbol{S}_x)t_\mathrm{p}\right]. \tag{6}$$

It describes the rotation of the spin around the effective field in the rotating frame, which lies in the xoz plane making an angle θ with the oz axis. That is $\tan\theta = \omega_1/\Delta\omega$. Thus, for $S = 1/2$, Eq. (6) can be rewritten as [20] (see Ref. [6], p. 24)

$$\boldsymbol{R} = \cos(\omega_\mathrm{e} t_\mathrm{p}/2) - 2\mathrm{i}\sin(\omega_\mathrm{e} t_\mathrm{p}/2)[\boldsymbol{S}_x \sin\theta + \boldsymbol{S}_z \cos\theta] \tag{7}$$

where $\omega_\mathrm{e} = \sqrt{(\Delta\omega)^2 + \omega_1^2}$ and $\sin\theta = \omega_1/\omega_\mathrm{e}$, $\cos\theta = \Delta\omega/\omega_\mathrm{e}$.

In the split Hamiltonian approximation we have for each step:

$$\tilde{\boldsymbol{R}}(n) = \exp\left[-\mathrm{i}\Delta\omega t_\mathrm{p} S_z/2n\right] \exp(-\mathrm{i}\omega_1 t_\mathrm{p} S_x/n) \exp(-\mathrm{i}\Delta\omega t_\mathrm{p} S_z/2n), \tag{8}$$

which corresponds to three successive rotations around the z, x, and z directions. It is easy to show that these successive rotations are equivalent to a single rotation given by:

$$\tilde{\boldsymbol{R}}(n) = \exp\left[-\mathrm{i}\tilde{\varphi}(n)(\cos\theta_n \boldsymbol{S}_z + \sin\theta_n \boldsymbol{S}_x)\right], \tag{9}$$

where the axis of rotation is again in the xoz plane but making an angle of θ_n with the oz axis, such that:

$$\begin{aligned} &\cos\theta_n = m_n^{-1}\cos(\omega_1 t_\mathrm{p}/2n)\sin(\Delta\omega t_\mathrm{p}/2n), \quad \sin\theta_n = m_n^{-1}\sin(\omega_1 t_\mathrm{p}/2n), \\ &m_n^2 = \sin^2(\omega_1 t_\mathrm{p}/2n) + \cos^2(\omega_1 t_\mathrm{p}/2n)\sin^2(\Delta\omega t_\mathrm{p}/2n). \end{aligned} \tag{10}$$

The angle of rotation about this axis is given by $\tilde{\varphi}(n)$:

$$\tilde{\varphi}(n) = 2\arccos\left[\cos(\omega_1 t_\mathrm{p}/2n)\cos(\Delta\omega t_\mathrm{p}/2n)\right]. \tag{11}$$

The form of Eq. (9) enables us to write $\boldsymbol{R}_n$ as

$$\boldsymbol{R}_n = \exp\left[-\mathrm{i}\varphi_n(S_z\cos\theta_n + S_x\sin\theta_n)\right] = \cos(\varphi_n/2) - 2\mathrm{i}\sin(\varphi_n/2)(S_x\sin\theta_n + S_z\cos\theta_n), \tag{12}$$

where $\varphi_n \equiv n\tilde{\varphi}(n)$, which is the full angle of rotation about the axis with angle of tilt given by θ_n. A comparison of Eq. (12) with the exact rotation operator, Eq. (7), shows that they are identical in form. We expect that as $n \to \infty$, $\boldsymbol{R}_n \to \boldsymbol{R}$. This is easy to show, since in this limit $\theta_n \to \theta$ and $\varphi_n \to \omega_\mathrm{e} t_\mathrm{p}$. That is, from Eqs. (10)

$$\lim_{n\to\infty}\tan\theta_n = \lim_{n\to\infty}\left[\tan(\omega_1 t_\mathrm{p}/2n)/\sin(\Delta\omega t_\mathrm{p}/2n)\right] = \omega_1/\Delta\omega$$

and

$$\lim_{n\to\infty}\varphi_n = \lim_{n\to\infty}\left\{2n\arccos\left[\cos(\omega_1 t_\mathrm{p}/2n)\cos(\Delta\omega t_\mathrm{p}/2n)\right]\right\} = \sqrt{\omega_1^2 + \Delta\omega^2}\, t_\mathrm{p} = \omega_\mathrm{e} t_\mathrm{p}. \tag{13}$$

For finite n we see that sufficient conditions for a good approximant are

$$\left(|\omega_1|t_p\right)^2 \ll 12n^2 \quad \text{and} \quad \left(\Delta\omega t_p\right)^2 \ll 24n^2, \tag{14}$$

such that $\tan(\omega_1 t_p/2n) \approx \omega_1 t_p/2n$ and $\sin(\Delta\omega t_p/2n) \approx \Delta\omega t_p/2n$, etc. For $|\omega_1|t_p$ of order of magnitude unity, small values of n are clearly sufficient for the first inequality. We have performed numerical calculations comparing the approximate and exact forms, for a range of values of $\Delta\omega$, ω_1, and t_p, and we find that they are consistent with the inequalities of Eqs. (14).

Next we wish to illustrate the application of split Hamiltonian theory (SHT) in predicting the outcome of pulse sequences utilizing arbitrary pulses. We consider a spin echo formed from two arbitrary pulses given by Eq. (12), and we compare them with the exact results obtained from Eq. (7). When we utilize small values of n (= 2, 4) we are able to obtain approximate analytical expressions. By splitting each of the two pulses into 2 (or 4) discrete pulses we obtain a series of discrete sub-echoes which in the $n \to \infty$ limit approach a continuum. Following standard procedures, the evolution of the spin density matrix, ρ leading to a primary spin-echo is given by:

$$\rho(t) \propto \exp[-\mathrm{i}H_0(t_1+t_2)]\,\boldsymbol{R}\exp(-\mathrm{i}\boldsymbol{H}_0 t_1)\boldsymbol{R}\boldsymbol{S}_z\boldsymbol{R}^{\dagger}\exp(\mathrm{i}\boldsymbol{H}_0 t_1)\boldsymbol{R}^{\dagger}\exp[\mathrm{i}\boldsymbol{H}_0(t_1+t_2)], \tag{15}$$

where, in the high-temperature approximation, $\rho_{eq} \propto S_z$. The observable signal is then proportional to

$$\langle S_- \rangle = \mathrm{Tr}[\rho(t)S_-]. \tag{16}$$

Using the exact equation, Eq. (7), yields

$$\langle S_- \rangle \propto 2\langle(\omega_1/\omega_e)^3 \sin^3(\omega_e t_p/2)\left[(\Delta\omega/\omega_e)\sin(\omega_e t_p/2) - \mathrm{i}\cos(\omega_e t_p/2)\right]\exp(\mathrm{i}\Delta\omega t_2)\rangle, \tag{17}$$

whereas using the approximate equation, Eq. (12), yields

$$\langle S_- \rangle \propto 2\langle |\boldsymbol{R}_{n,12}|^2 \boldsymbol{R}_{n,12}\boldsymbol{R}^*_{n,11}\exp(-\mathrm{i}\Delta\omega t_2)\rangle,$$

where

$$\boldsymbol{R}_{n,12} = -\mathrm{i}\sin\theta_n \sin(\varphi_n/2)$$

and

$$\boldsymbol{R}_{n,11} = \cos(\varphi_n/2) - \mathrm{i}\cos\theta_n \sin(\varphi_n/2). \tag{18}$$

Here $\langle\,\rangle$ denotes an averaging over an inhomogeneous distribution of resonance frequencies, ω_0. We used the Gaussian distribution:

$$f(\omega_0) = \frac{1}{\sqrt{2\pi\Delta_G^2}}\exp\left[-\left(\omega_0 - \omega_0^0\right)^2/2\Delta_G^2\right], \tag{19}$$

where ω_0^0 is the mean value of ω_0 and Δ_G^2 is the mean square deviation. Numerical simulations have demonstrated that Eqs. (18) are appropriate, and only small values of n are needed to obtain convergence. For example, we find that for pulses that obey: $\omega_1 t_p \leqslant \pi/2$, good approximations are achieved with $n = 2$ if $\Delta_G/4\omega_1 \ll 1$ consistent with the inequalities of Eq. (14). Thus, in EPR experiments with $\omega_1/\gamma = B_1 \approx 10$ G, good numerical results are obtained with $\Delta_G \leqslant 20$ G (cf. Fig. 1). When Δ_0 is larger, or $\omega_1 t_p \geqslant \pi$, then a larger value of n is required.

The numerical calculations of the primary spin-echo signal also show a strong dependence of the shape of the echo signal on ω_1, t_p, and Δ_G. In the limit of non-selective pulses, the shape of the primary spin-echo is well-known, and is readily obtained from Eq. (17):

$$\langle S_- \rangle \propto -\mathrm{i}\sin^2(\omega_1 t_p/2)\sin(\omega_1 t_p)\cos\left[(\omega_0^0 - \omega)t_2\right]\exp\left(-\Delta_G^2 t_2^2/2\right), \tag{20}$$

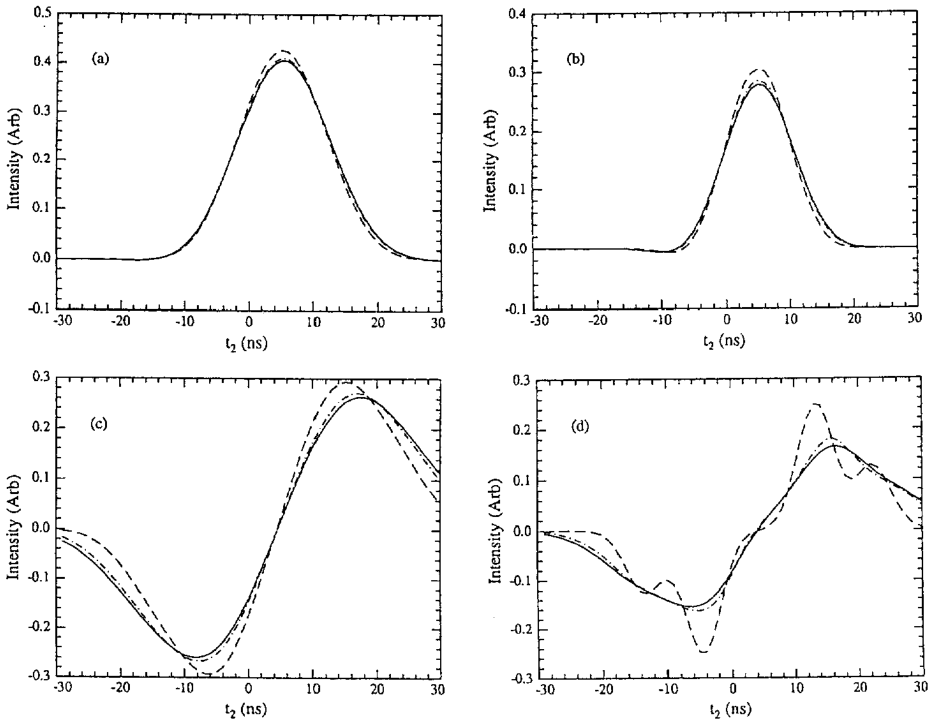

Fig. 1. Convergence of the SHT for a spin-echo formed from two arbitrary pulses as a function of t_2: (a) and (b) are for two $\pi/2$ pulses; (c) and (d) are for two π pulses. In cases (a) and (c) $\Delta_G/\omega_1 = 1$, and in cases (b) and (d) $\Delta_G/\omega_1 = 2$. (———) shows the exact result, (— — —) shows the $n = 2$ approximation, and (—·—·—) shows the $n = 4$ approximation. In these figures $\omega_1/\gamma_e = 10$ G for ESR and $\Delta\omega = \omega_0^0 - \omega = 0$. (These results scale using the dimensionless variables: $\omega_1 t_p$, Δ_G/ω_1, and $\omega_1 t_2$.)

which predicts the echo maximum at $t_2 = 0$ and a Gaussian shape with rms width, Δ_G^{-1}. When $\omega \neq \omega_0^0$, then the echo signal is modulated at the difference frequency $\omega_0^0 - \omega \equiv \Delta\omega$. However, in the case of arbitrary pulses, the shape of the echo signal can be rather complex, even when $\omega = \omega_0^0$. The overall echo signal becomes broader compared to that predicted by Eq. (20). In fact, for $\Delta_G t_p > 1$ the echo width becomes proportional to t_p (i.e. of order t_p). The nature of this broadening can readily be studied using SHT. As we have already noted, when each pulse is described by a sequence of close non-selective pulses, any pairs of two short sub-pulses from the two arbitrary pulses will produce an echo, and these echoes will refocus at different acquisition times for which $|t_2| \leqslant t_p$. Using SHT we can readily write down the results for $n = 2$. We obtain:

$$\langle S_- \rangle \propto -(i/4)\sin^3(\omega_1 t_p/2) \sum_{m=1}^{5} J_k \langle \exp[-i\Delta\omega(t_2 - k t_p/4)] \rangle, \tag{21}$$

where $k = 2m - 5$. The coefficients J_k are:

$$J_{-3} = -\sin^2(\omega_1 t_p/4), \quad J_{-1} = \cos^2(\omega_1 t_p/4) - 3\sin^2(\omega_1 t_p/4),$$
$$J_1 = 3\cos(\omega_1 t_p/2), \quad J_3 = 3\cos^2(\omega_1 t_p/4) - \sin^2(\omega_1 t_p/4), \quad J_5 = \cos^2(\omega_1 t_p/4). \tag{22}$$

Thus, for the $n = 2$ approximant, the echo signal is the superposition of five terms refocusing at $t_2 = -3t_p/4$, $-t_p/4$, $+t_p/4$, $3t_p/4$, and $5t_p/4$, with intensities given by Eqs. (22), respectively. The overall width should then be of order $2t_p + 2/\Delta_G$, which becomes $2t_p$ for $\Delta_G t_p \gg 1$. We have also obtained the expressions for the $n = 4$ approximant. This consists of 13 terms which refocus between $t_2 = -13t_p/8$ and $t_2 = +11t_p/8$ for a total extent of $3t_p$, but with the terms refocusing nearest $t_2 \approx 0$ being largest in intensity and falling off as they deviate more from zero. For an accurate approximation, we want an n such that $(\Delta_G t_p)^2 \ll 24n^2$ [cf. Eq. (14)]. In this case, the spacing between component refocusing terms becomes smaller than the Δ_G^{-1} width of each component and a smooth but broad echo shape is obtained (cf. Fig. 1).

In particular, we find that for $\omega_1 t_p \leqslant \pi/2$ and $\Delta_G \leqslant \omega_1$, choosing $n = 2$ provides a reasonably good description of the shape of the echo signal, again consistent with Eq. (14). Otherwise a somewhat larger value of n would be required for good accuracy (cf. Fig. 1).

3. Nuclear modulation of the electron-spin-echo signal

The basic features of the electron-spin-echo (ESE) signal modulated by the anisotropic hfi can be illustrated with the simple case of one electron spin S, with $S = 1/2$, and one nuclear spin I, with $I = 1/2$. In this case the spin Hamiltonian in the rotating frame is $H = H_0 + H_1$ with

$$H_0 = \Delta\omega S_z - \omega_n I_z + T_{zz} S_z I_z + T_{zx} S_z I_x, \quad H_1 = \omega_1 (S_x \cos\psi + S_y \sin\psi). \tag{23}$$

Here $\omega_n = \gamma_n B_0$ and it is the nuclear Larmor frequency, while T_{zz} and T_{zx} are components of the hf tensor, and ψ is the phase angle of the radiation field. The eigenvalues and eigenfunctions of H_0 given by Eq. (23) are well-known, and may readily be written in terms of the simple product basis states, i.e. the $|S_z, I_z\rangle$ basis. Thus $\exp(iH_0 t_p/n)$ in Eq. (4) can be easily written in the basis that diagonalizes H_0, i.e. the H_0 basis, and transformed back to the $|S_z, I_z\rangle$ basis. The $\exp(iH_1 t_p/n)$ operator is readily written in the $|S_z, I_z\rangle$ basis (and then transformed into the H_0 basis). Thus the R_2 operator of Eq. (4a) can readily be calculated in either basis, and we give details elsewhere.

In the previous section, we showed that the approximation of R_2 (i.e. $n = 2$) is able to describe fairly well the response of a spin system to exciting pulses when the inhomogeneous broadening is not very large, e.g. for $\pi/2$ pulses R_2 is accurate if $\Delta_G \leqslant 20$ G when $B_1 \sim 10$ G. For greater Δ_G and/or pulses yielding larger nominal angles of rotation we may expect that the R_2 solution can provide useful insights (i.e. is "semi-quantitative") without necessarily being quantitatively accurate. Larger values of n may always be used in numerical computations, but they lead to more complicated equations from which it is difficult to extract useful insights, so we restrict our attention to the $n = 2$ analytical solutions.

It is well-known that the nuclear modulation of an ESE signal depends upon the nature of the excitation of a spectrum by microwave pulses [1]. Again we use two equal pulses of duration, t_p, which are separated by a time interval t_1, and the acquisition time after the second pulse is $t_1 + t_2$.

Our results ($n = 2$) again show that the primary ESE is represented as the sum of five echo terms, which refocus at slightly different values of t_2. Here we obtain

$$\langle S_- \rangle \propto -(i/4) \sin^3(\omega_1 t_p/2) \exp[i(2\psi_2 - \psi_1)] \sum_{m=1}^{5} J_k(t_2 - k t_p/4), \tag{24}$$

where again $k = (2m - 5)$, with ψ_1 and ψ_2 the phases of the first and second pulses respectively. For example, the term J_5, which refocuses the latest, i.e. at $t_2 = 5t_p/4$, is given by

$$J_5 = 2\cos^2(\omega_1 t_p/4) \Bigg\{ k_+ \bar{A}(t_2 - 5t_p/4) + k_- F(t_2 - 5t_p/4) + (k/4) \sum_{i=1}^{6} M_i[(t_1 + 3t_p/2), (t_2 - 5t_p/4)] \Bigg\} \exp\left[-\frac{1}{2} \Delta_G^2 (t_2 - 5t_p/4) \right], \tag{25}$$

where $\bar{A}(t) = \cos(\omega_+ t_2)$, and it is the allowed ESR signal; $F(t) = \cos(\omega_- t_2)$ and it is the forbidden ESR signal, whereas the M_i are the nuclear modulation signals given by:

$$M_1(t_1, t_2) = \cos(\omega_\alpha t_1 + \omega_- t_2), \quad M_2(t_1, t_2) = \cos(\omega_\beta t_1 - \omega_- t_2),$$
$$M_3(t_1, t_2) = \cos(\omega_\alpha t_1 + \omega_+ t_2), \quad M_4(t_1, t_2) = \cos(\omega_\beta t_1 + \omega_+ t_2),$$
$$M_5(t_1, t_2) = -\cos(2\omega_+ t_1 + \omega_+ t_2), \quad M_6(t_1, t_2) = -\cos(2\omega_- t_1 + \omega_- t_2) \tag{26}$$

The key nuclear modulation frequencies are:

$$\omega_\alpha = \left[(A/2 - \omega_n)^2 + |B|^2/4\right]^{1/2},$$
$$\omega_\beta = \left[(A/2 + \omega_n)^2 + |B|^2/4\right]^{1/2}, \tag{27}$$

with $\omega_\pm = (\omega_\alpha \pm \omega_\beta)/2$, and we have let $T_{zz} = A$ and $T_{zx} = B$. The coefficients are given by $k = (\omega_n |B| / \omega_\alpha \omega_\beta)^2$ and $k_\pm = (1 - k/2 \pm \sqrt{1-k})/2$. The terms in curly brackets in Eq. (25) form just the expression obtained from two non-selective pulses, except that the echo maximum is formed at $t_2 = 5t_p/4$, and the nuclear modulation terms are all phase shifted by the amount $3t_p/2$ in their t_1 dependence.

The other terms, which refocus earlier than J_2, have much more complex dependence on t_1. The nuclear modulation terms have different and more complex phase shifts in t_1 and different and more complicated dependences of their amplitudes on the coefficients k, $k_\pm$, and $\omega_\alpha t_p$ and $\omega_\beta t_p$, as well as different dependences on $\omega_1 t_p$. The fact that the J_k terms refocus between $t_2 = -3t_p/4$ and $5t_p/4$ leads to a broadening of the echo signal, as we have seen, and the more complex behavior of the echo modulation especially near the center of the echo means that the modulation will be better pronounced on the tail of the echo, an observation that is well-known from experiment. Thus, even at a low order approximation ($n = 2$), SHT enables the interpretation of key features of the echo signal, which are absent from descriptions based on the approximation of non-selective pulses.

4. Pulse adjustable spectroscopies

In recent years a number of new pulse sequences have been developed that substantially improve resolution and sensitivity in the study of nuclear modulation [2–4,12,20–25]. We shall be concerned with a type of pulse sequence, wherein nuclear modulation is developed during the action of a pulse instead of during the time interval between pulses. In particular, we shall consider the 2 + 1 pulse sequence in which an arbitrary pulse is inserted between two non-selective pulses [2] (cf. Fig. 2b). The effect of the arbitrary pulse upon the spin-echo formed by the two non-selective pulses is then studied. This experiment has recently been developed into a 2D format as "2 + 1 SECSY" [3]. We shall also consider a variant, the 1 + 2 pulse sequence in which the arbitrary pulse precedes two non-selective pulses (cf. Fig. 2a), and its effect on the spin-echo formed by the two non-selective pulses is studied [4]. Again we utilize SHT for $n = 2$.

We write the results in a compact notation very similar to that previously used by Gamliel and Freed [26]. Note that at the $n = 2$ level, the arbitrary pulse is represented by two non-selective pulses of duration $t_p/2$ and two non-selective pulses of infinitesimal duration. Thus general expressions for four-pulse sequences may be used [27]. We first consider the "1 + 2 SECSY" experiment using the spin Hamiltonian of Eq. (23). We obtain the signal as:

$$\langle S_- \rangle \propto -(i/4) \exp\left[i(2\psi_4 - \psi_3)\right] \sin\theta_3 (1 - \cos\theta_4) \sum_{k=0}^{1} J_k, \tag{28}$$

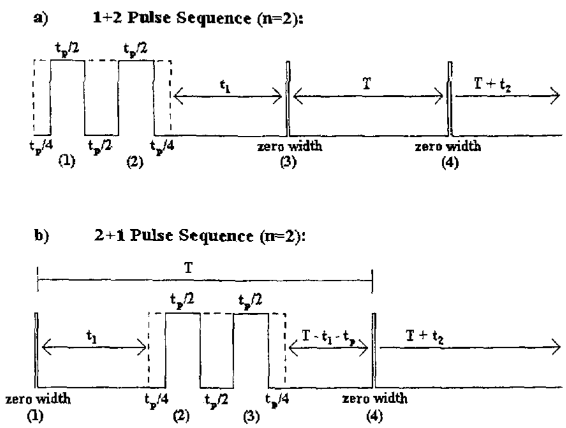

Fig. 2. (a) The "1 + 2" pulse sequence in the $n = 2$ SHT approximation; (b) the "2 + 1" pulse sequence in the $n = 2$ SHT approximation. Note that this approximation corresponds to four non-selective pulses, wherein the "+ 1" pulse is composed of two non-selective pulses of width $t_p/2$, which necessarily have the same phase. The phases ψ_1, ψ_3, and ψ_4 in Eqs. (28) and (30) correspond to the pulses as numbered in (a) and (b) respectively.

with

$$J_0 = \cos^2\theta_1 \langle \sum_{\text{all indices}} \exp(i\omega_{\alpha\gamma}\tau_4) \exp(i\omega_{\gamma'\alpha'}\tau_3) M_{\alpha\gamma} M^\dagger_{\gamma\alpha'} M_{\alpha'\gamma'} M^\dagger_{\gamma'\alpha} \rangle, \tag{29a}$$

$$J_1 = \frac{-\sin^2\theta_1}{4} \langle \sum_{\text{all indices}} \exp(i\omega_{\alpha\gamma}\tau_4) \exp(i\omega_{\alpha''\alpha'}\tau_3) \{ [\exp(i\omega_{\alpha''\alpha'}\tau_2) \exp(i\omega_{\gamma'\alpha'}\tau_1)$$
$$+ \exp(i\omega_{\gamma''\gamma'}\tau_2) \exp(i\omega_{\gamma''\alpha''}\tau_1)] + [\exp(i\omega_{\alpha''\alpha'}\tau_2) + \exp(i\omega_{\gamma''\gamma'}\tau_2)] \exp(i\omega_{\alpha''\gamma'}\tau_1) \}$$
$$\times M_{\alpha\gamma} M^\dagger_{\gamma\alpha'} M_{\alpha'\gamma'} M^\dagger_{\gamma'\alpha''} M_{\alpha''\gamma''} M^\dagger_{\gamma''\alpha} \rangle. \tag{29b}$$

In these equations we have $\tau_1 = t_p/2$, $\tau_2 = t_1 + t_p/4$, $\tau_3 = T$, $\tau_4 = T + t_2$ (cf. Fig. 2a). Also θ_3 and θ_4 represent the angles of rotation of the two non-selective pulses, and $\theta_1 = \theta_2 = \omega_1 t_p/2$. The subscripts α, γ etc. refer to the eigenstates of H_0 Eq. (23), where α, α', α'', refer only to states with $M_s = +1/2$ and γ, γ', γ'' etc. refer only to states with $M_s = -1/2$. That is, α is either eigenstate a or b and γ is either c or d. Their well-known eigenvalues are $E_a = \Delta\omega/2 + \omega_\alpha$, $E_b = \Delta\omega/2 - \omega_\alpha$, $E_c = -\Delta\omega/2 + \omega_\beta$, $E_d = -\Delta\omega/2 - \omega_\beta$ with the ω_α and ω_β given by Eqs. (27). In the above equations $\omega_{\alpha\gamma} = E_\alpha - E_\gamma$, etc. The four matrix elements $M_{\alpha\gamma}$ of M (with $M^\dagger$ its Hermitian adjoint) are given by $M_{ac} = M_{bd} = m_1$ and $M_{ad} = -M_{bc} = -m_2$ where: $m_1^4 = k_+$, $m_2^4 = k_-$, and $m_1^2 m_2^2 = k/4$.

A careful examination of the J_0 term in Eq. (28) shows that it is just the signal obtained from the two non-selective pulses. Thus it is exactly of the form of Eq. (25) with its allowed, forbidden, and nuclear modulation signals. The echo maximum comes at $\tau_3 = \tau_4$ equivalent to $t_2 = 0$, as expected for this basic signal. The new term(s) are given by J_1, and they are more complicated. In the 1 + 2 experiment, one steps out $t_1 = \tau_2 - t_p/4$. Thus the modulation in τ_2 just involves frequencies of type $\omega_{\alpha''\alpha'}$ and $\omega_{\gamma''\gamma'}$. These are nuclear coherences when $\alpha'' \neq \alpha'$ or $\gamma'' \neq \gamma'$. If $\alpha'' = \alpha'$ (or $\gamma'' = \gamma'$), then we have zero-order coherences which show no modulation of the echo with t_1 (or τ_2). Thus we see that the arbitrary first pulse may be used to generate nuclear coherence, which is converted to $M_s = \pm 1$ coherence by the first non-selective pulse and then refocused by the second non-selective pulse. Also, we see that by selecting $2\theta_1 = \omega_1 t_p = \pi$, 3π, 5π, etc., we can suppress the J_0 term and maximize the J_1 term. Note also that the precise location of the echo maximum is shifted to $t_2 = t_p/2$ for some of the terms in J_1 and to $-t_p/2$ for the others.

Note that since one has $\omega_1 t_p \approx \pi$ for a maximum nuclear coherence signal, and it is not necessarily true that $|\omega_1| > |\omega_\alpha|, |\omega_\beta|$, then we do not expect the $n = 2$ solution to be a good quantitative representation [28]. Rather we look to this solution as a rough approximation with, however, key qualitative features that are useful in guiding the design of the experiment and its preliminary interpretation.

In the same spirit, we consider "2 + 1 SECSY" of Fig. 2b and we obtain:

$$\langle S_- \rangle = -(i/16) \exp[i(2\psi_4 - \psi_1)] \sin \theta_1 (1 - \cos \theta_4) \sum_{k=0}^{2} J_k, \tag{30}$$

$$J_0 (1 + \cos \theta_2)^2 \langle \sum_{\text{all indices}} \exp(i\omega_{\alpha\gamma}\tau_4) \exp\left[i\omega_{\gamma'\alpha'}(\tau_3 + \tau_2 + \tau_1)\right] M_{\alpha\gamma} M^\dagger_{\gamma\alpha'} M_{\alpha'\gamma'} M^\dagger_{\gamma'\alpha} \rangle, \tag{31a}$$

$$J_1 = (1 - \cos \theta_2)^2 \langle \sum_{\text{all indices}} \exp(i\omega_{\alpha\gamma}\tau_4) \exp(i\omega_{\gamma'''\alpha'}\tau_3) \exp(i\omega_{\alpha'''\gamma'}\tau_2) \exp(i\omega_{\gamma''\alpha''}\tau_1)$$
$$\times M_{\alpha\gamma} M^\dagger_{\gamma\alpha'} M_{\alpha'\gamma'} M^\dagger_{\gamma'\alpha''} M_{\alpha''\gamma''} M^\dagger_{\gamma''\alpha'''} M_{\alpha'''\gamma'''} M^\dagger_{\gamma'''\alpha} \rangle, \tag{31b}$$

$$J_2 = -\sin^2 \theta_2 \langle \sum_{\text{all indices}} \exp(i\omega_{\alpha\gamma}\tau_4) \exp(i\omega_{\gamma''\alpha'}\tau_3) \left[\exp(i\omega_{\alpha''\alpha'}\tau_2) \exp(i\omega_{\gamma'\alpha'}\tau_1)\right.$$
$$\left. + \exp(i\omega_{\gamma''\gamma'}\tau_2) \exp(i\omega_{\gamma''\alpha''\tau_2})\right] M_{\alpha\gamma} M^\dagger_{\gamma\alpha'} M_{\alpha'\gamma'} M^\dagger_{\gamma'\alpha''} M_{\alpha''\gamma''} M^\dagger_{\gamma''\alpha} \rangle. \tag{31c}$$

Here, $\tau_1 = t_1 + t_p/4$, $\tau_2 = t_p/2$, $\tau_3 = T - t_1 - 3t_p/4$, and $\tau_4 = T + t_2$. Also $\theta_2 = \theta_3 = \omega_1 t_p/2$. Thus the main echo given by J_0, of the same form as Eq. (25), has its maximum at $\tau_4 = \tau_1 + \tau_2 + \tau_3$ corresponding to $t_2 = 0$, as it should. The new terms J_1 and J_2 have echo maxima at $t_2 = -t_p$ and $-t_p/2$ respectively, ignoring nuclear modulation. These terms are studied as a function of t_1, so they will show the modulation from both τ_1 and τ_3. These are characteristic nuclear modulation terms. For example, writing out the product of the 4 exponentials in Eq. (31b) as a sum in the exponent and recombining, we find the modulation in t_1 and t_2 to be given by:

$$\exp(i\omega_{\alpha\gamma} t_2) \exp\left[i(\omega_{\gamma''\alpha''} - \omega_{\gamma'''\alpha'}) t_1\right],$$

However, the amplitude and phase of each such modulation term will depend upon the value of T and t_p according to:

$$\exp\left[i(\omega_{\alpha\gamma} + \omega_{\gamma'''\alpha'})T + i(2\omega_{\alpha'''\gamma'} - 3\omega_{\gamma'''\alpha'} + \omega_{\gamma''\alpha''}) t_p/4\right].$$

This may be at least partial explanation of the fact that by "2 + 1 SECSY" one can tune in or out low frequency versus high frequency modulations. Note that the J_1 term can be optimized relative to the J_0 term by letting $2\theta_2 = \omega_1 t_p = 2\pi$, which is consistent with experimental observation, whereas the J_2 term would also be suppressed by this condition.

Again we regard this $n = 2$ approximation as hardly quantitative, especially with $\omega_1 t_p \approx 2\pi$. Its primary value is in providing insight into the experiment.

We plan in a future publication [28], to provide more details, including practical convergence criteria, to these approximate solutions for 1 + 2 and 2 + 1 SECSY as well as other cases of pulse adjustable spectroscopies including multiple quantum coherence in NMR [7] and in ESR [5], as well as its application to time domain experiments on spin polarization in radical pairs [29]. Finally we note that SHT would also be appropriate to obtain approximate analytic forms for optical pulse experiments.

Acknowledgement

We wish to thank Drs. Z. Liang, A. Raitsimring, and P. Borbat and Mr. John Lee for helpful discussions. This work was supported by NSF Grant CHE9313167 and NIH Grant RR07126.

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