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Transient Decay of Longitudinal Magnetization in Heterogeneous Spin Systems under Selective Saturation. III. Solution by Projection Operators*

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A general method of solving equations governing the transient response of heterogeneous spin systems to continuous and pulsed RF saturation using the projection-operator technique is outlined. An effective rate equation is derived in which there is natural separation of relaxation and source terms. Our previously derived implicit solution to the coupled Bloch equations is reformulated using this more general approach, which avoids some of the restrictive assumptions made earlier. With this formulation, we provide an analytical and explicit solution to the full set of coupled Bloch equations with no additional assumptions or restrictive conditions attached limiting their general validity. The results obtained with this new method of solution are compared with the results previously obtained by the Laplace-transform technique for heat-denatured albumin. © 1993 Academic Press, Inc.

INTRODUCTION

In two previous articles (*1*, *2*) (to be referred to as I and II, respectively), we described the general solutions for the coupled equations for the response of a heterogeneous spin system subjected to selective RF saturation either by continuous off-resonance irradiation (*1*) or by on-resonance binomial pulses (*2*). Each of these solutions is based on a set of coupled Bloch equations formulated according to a binary spin-bath model (*3–6*). Two fundamental problems important for future developments remained unsolved from these studies. The first concerns the complexity and the implicitness of the transient solutions to the theoretical model presented. The second concerns the validity of the conventional Bloch equations when applied to saturation in solids (*7*, *8*). In this article, we address the first problem by proposing an alternative method for solving the multidimensional coupled differential equations and will address the second problem in a subsequent article (*9*) by proposing an alternative formulation of equations of motion for the spin-bath model.

The first problem stems from the method of solution used in our previous attempts. The time-honored Laplace-transform technique (*10*), when applied to problems with dimensionality exceeding three, tends to give analytical results that are algebraically complex and are often implicit in nature. This is rather unsettling since little, although not entirely negligible, physical insight can be derived from them until numerical results are generated. Moreover, this algebraic complexity necessitates reducing the problem to a smaller number of dimensions by restricting the validity of the solutions to certain limiting conditions. For instance, in I, the solutions were restricted to the conditions for which the saturation RF is sufficiently far from the water resonance (*11*). To overcome this problem, we propose using an alternative method called the projection-operator (PO) technique, first advanced by Zwanzig (*12*) and by Mori (*13*) and used by Adler (*14*) in a manner similar to that proposed below. This technique provides a powerful and elegant means for deriving explicit and analytically simple solutions to complicated problems with multiple degrees of freedom (as typically would occur in many-body problems). The power of this technique resides in the fact that the projection operator reduces the solution of the coupled multidimensional problem to one with fewer degrees of freedom (i.e., in this case, a one-dimensional problem), the solution of which is usually quite tractable. This feature is particularly well suited to our problem, in which only the longitudinal component of the free water proton magnetization M_{zA} can be dynamically monitored by experiment.

In the following sections, we solve the Bloch equations in their conventional form (*1*, *11*) using the PO technique under both continuous and pulsed saturation without any simplifying assumptions. For continuous saturation, the PO used, in the context presented herein, produces a single equation for the relevant variable, M_{zA} in which intrinsic relaxation and sources of magnetization transfer are naturally separated. A remarkably simple solution is attainable under this condition because, under continuous saturation, the time lapse between the onset of saturation and observation is so

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long that asymptotic solution of the longest time constant is, for all practical purpose, all one needs. In saturation with binomial pulses, since the pulse width is on the order of a few milliseconds, contributions from transient components of shorter time constants may not entirely negligible, although one may still ignore the faster transients to simplify matters. The solutions obtained in these circumstances are then compared with those obtained in I and II for heat-denatured albumin using the same spin-bath parameters derived previously.

SOLUTION TO THE CONVENTIONAL COUPLED BLOCH EQUATIONS UNDER CONTINUOUS RF IRRADIATION

By following the same convention as I and II, the Bloch equations which describe the heterogeneous spin system modeled after a pair of coupled spin baths in the presence of an RF field can be written in the rotating reference frame in dimensionless parameters and variables as

$$\frac{d(u_\varsigma)}{d\tau} + \beta_\varsigma u_\varsigma + \delta_\varsigma v_\varsigma = 0 \qquad [1a]$$

$$\frac{d(v_\varsigma)}{d\tau} + \beta_\varsigma v_\varsigma - \delta_\varsigma u_\varsigma + (1 - 2w_\varsigma) = 0 \qquad [1b]$$

$$\frac{dw_A}{d\tau} + (\alpha_A + \alpha_X)w_A - \alpha_X w_A + \frac{v_A}{2} = 0 \qquad [1c]$$

$$\frac{dw_B}{d\tau} + \left(\alpha_B + \frac{\alpha_X}{f}\right)w_B - \frac{\alpha_X}{f} w_A + \frac{v_B}{2} = 0, \qquad [1d]$$

where

$$u_\varsigma = \frac{M_\varsigma^x}{M_\varsigma^{z0}},\ v_\varsigma = \frac{M_\varsigma^y}{M_\varsigma^{z0}},\ w_\varsigma = \frac{M_\varsigma^{z0} - M_\varsigma^z}{2M_\varsigma^{z0}},\ \varsigma = \text{A, B}, \qquad [2]$$

with M_ς^z and M_ς^{z0} denoting the longitudinal magnetization and its equilibrium value, respectively, of the A or B spins. The transverse components of the magnetization that are in phase and 90° out of phase with respect to the applied RF field, respectively, are u and v. The other dimensionless parameters are defined by $\tau = \omega_1 t$, f = molar ratio of the B spins to A spins,

$$\alpha_{A,B} = 1/\omega_1 T_{1A,B},\ \alpha_X = r_X/\omega_1,\ \beta_{A,B} = 1/\omega_1 T_{2A,B}, \qquad [3a]$$

and

$$\delta_{A,B} = \Delta\omega_{A,B}/\gamma\omega_1;\quad \delta\omega_{A,B} = \omega - \omega^0_{A,B}, \qquad [3b]$$

where $\omega_1 = \gamma B_1$, $T_{1A,B}$ and $T_{2A,B}$ are the intrinsic relaxation times of the A and B spins, r_X is the cross-relaxation rate, and $\Delta\omega_{A,B}$ are the frequency offsets of the RF field with respect to the A and B resonances, respectively. To simplify matters somewhat, we assume $\delta_A = \delta_B = \delta$, which amounts to ignoring the small difference in chemical shift between the A and B spins.

To solve [1], we define

$$\mathbf{X} = \text{col}\{u_B, v_B, w_B, u_A, v_A, w_A\}. \qquad [4]$$

We then rewrite [1] as

$$\frac{d}{d\tau}\mathbf{X} + \mathbf{RX} = \mathbf{Y}, \qquad [5]$$

with $\mathbf{R}$ and $\mathbf{Y}$ defined, respectively, as

$$\mathbf{R} = \begin{bmatrix} \beta_B & \delta & 0 & 0 & 0 & 0 \\ -\delta & \beta_B & -2 & 0 & 0 & 0 \\ 0 & 1/2 & \alpha_B + \alpha_X/f & 0 & 0 & -\alpha_X/f \\ 0 & 0 & 0 & \beta_A & \delta & 0 \\ 0 & 0 & 0 & -\delta & \beta_A & -2 \\ 0 & 0 & -\alpha_X & 0 & 1/2 & \alpha_A + \alpha_X \end{bmatrix} \qquad [6]$$

$$\mathbf{Y} = \text{col}\{0, -1, 0, 0, -1, 0\} = -\mathbf{e}_2 - \mathbf{e}_5, \qquad [7]$$

where we have defined the unit vectors $\{\mathbf{e}_j\} = \text{col}\{\delta_{ij}\}$ as indicated by $\mathbf{e}_2$ and $\mathbf{e}_5$ above. The initial magnetizations for both the A spins and the B spins are assumed to be longitudinal with $w_A(0) = \eta_A$ and $w_B(0) = \eta_B$, respectively. Thus, $\mathbf{X}(0) = \eta_B\mathbf{e}_3 + \eta_A\mathbf{e}_6$. We now define a complementary pair of projection operators, p and q, as

$$p = e_6 e_6^T,\quad q = \mathbf{1} - p, \qquad [8]$$

so that $p^2 = p$, $q^2 = q$, $pq = qp = 0$, and $p\mathbf{X} = \text{col}\{0, 0, 0, 0, 0, w_A\}$. Given these properties satisfied by p and q, we can derive (for details see Appendix A) an inhomogeneous equation for w_A, in which the u_B, u_A, v_B, v_A, and w_B dependencies are eliminated from Eq. [1]. The result is given as

$$\frac{dw_A}{d\tau} + (\alpha_A + \alpha_X)w_A + \int_0^\tau \varphi(\tau - s)w_A(s)ds = \xi(\tau), \qquad [9a]$$

where the function φ, bearing a superficial resemblance to the memory term of the Langevin equation as a consequence of the fluctuation–dissipation theorem (*13*), is given by

$$\varphi(\tau) \equiv (\dot{\phi}^T(\tau)\cdot q\mathbf{R}\mathbf{e}_6) \qquad [9b]$$

$$\xi(\tau) \equiv -\eta_B\dot{\phi}^T(\tau)\cdot\mathbf{e}_3 + \int_0^\tau \dot{\phi}^T(\tau - s)\cdot(\mathbf{e}_2 + \mathbf{e}_5)ds \qquad [9c]$$

$$\phi(\tau) = \exp(-\tau q\mathbf{R}^T)\mathbf{e}_6, \qquad [9d]$$

where "˙" refers to a time derivative. In this representation, $\xi(\tau)$ represents a production term for the appearance of magnetization transfer from the B spins, while the apparent relaxation rate of the A spins is determined by the terms $\alpha_A + \alpha_X$ and $\varphi(\tau)$. For a time scale long compared to the inverse of all the nonzero eigenvalues of $q\mathbf{R}^T$, or for $\tau \gg \lambda_j^{-1}$, $j = 1, 2, 3, 4, 5$, w_A will satisfy an asymptotic equation given by

$$\left(\frac{d}{d\tau} + \alpha_{app}\right) w_A = \xi(\infty), \qquad [10]$$

where α_{app} is the apparent relaxation rate defined as

$$\alpha_{app} = \alpha_A + \alpha_X + \int_0^\infty \varphi(s)ds. \qquad [11]$$

Solving [10], one gets

$$w_A(\tau) = \left[w_A(0) - \frac{\xi(\infty)}{\alpha_{app}} \right] e^{-\alpha_{app}\tau} + \frac{\xi(\infty)}{\alpha_{app}}. \qquad [12]$$

As is shown in Appendix B, $\phi(\tau)$ is explicitly evaluated by an appropriate set of eigenvectors and eigenvalues for the matrix $q\mathbf{R}^T$. Let $\{\mathbf{v}_l^j, \mathbf{v}_r^j\}$, $j = 0, 1, 2, 3, 4, 5$, denote such a set of left and right eigenvectors which correspond to the eigenvalues $\lambda_0 = 0, \lambda_1, \lambda_2, \ldots, \lambda_5$, respectively. We can then write

$$\varphi(\tau) = -\sum_{j=1}^{5} \lambda_j e^{-\lambda_j \tau} (\mathbf{v}_l^j \cdot \mathbf{v}_r^j)(\mathbf{v}_r^{jT} \cdot q\mathbf{R}\mathbf{e}_6) \qquad [13]$$

$$\xi(\tau) = \xi(\infty) + \sum_{j=1}^{5} e^{-\lambda_j \tau} (\mathbf{v}_l^{jT} \cdot \mathbf{e}_6)[\eta_B \lambda_j (\mathbf{v}_r^{jT} \cdot \mathbf{e}_3) - \{\mathbf{v}_r^{jT} \cdot (\mathbf{e}_2 + \mathbf{e}_5)\}] \qquad [14]$$

with

$$\xi(\infty) = -(\mathbf{v}_l^{0T} \cdot \mathbf{e}_6)[\mathbf{v}_r^{0T} \cdot (\mathbf{e}_2 + \mathbf{e}_5)] = -\mathbf{v}_r^{0T} \cdot (\mathbf{e}_2 + \mathbf{e}_5), \qquad [15]$$

the second equality in [14] resulting from $\mathbf{e}_6^T q\mathbf{R}^T = 0$, which implies that $\mathbf{v}_l^0 = \mathbf{e}_6^T$. Similarly, $\int_0^\infty \varphi(s)ds$ may be written as

$$\int_0^\infty \varphi(s)ds = \mathbf{v}_r^{0T} \cdot q\mathbf{R}\mathbf{e}_6$$

so that

$$\alpha_{app} = \alpha_A + \alpha_X + \mathbf{v}_r^{0T} \cdot q\mathbf{R}\mathbf{e}_6. \qquad [16]$$

To find $\mathbf{v}_r^{0T}$, the right-sided eigenvector of $q\mathbf{R}^T$ with $\lambda_0 = 0$, we note

$$q\mathbf{R}^T \mathbf{v}_r^0 = \mathbf{0}. \qquad [17]$$

Let $\mathbf{v}_r^0 = \text{col}\{a, b, c, d, e, 1\}$. It is straightforward to solve the simultaneous equations in [17]. The results for a, b, c, d, and e are given by

$$a = -\frac{\alpha_X \delta_B/2}{\beta_B + (\alpha_B + \alpha_X/f)(\delta^2 + \beta_B^2)},$$

$$b = -\frac{\alpha_X \beta_B/2}{\beta_B + (\alpha_B + \alpha_X/f)(\delta^2 + \beta_B^2)},$$

$$c = \frac{\alpha_X(\delta^2 + \beta_B^2)}{\beta_B + (\alpha_B + \alpha_X/f)(\delta^2 + \beta_B^2)},$$

$$d = -\frac{1}{2}\frac{\delta}{\delta^2 + \beta_A^2}, \quad e = -\frac{1}{2}\frac{\beta_A}{\delta^2 + \beta_A^2}. \qquad [18]$$

It follows from [6] that $\mathbf{v}_r^{0T} \cdot q\mathbf{R}\mathbf{e}_6 = -[2e + (\alpha_X/f)c]$, which according to [11] yields the apparent relaxation rate

$$\alpha_{app} = \alpha_A + \alpha_X - \frac{\alpha_X^2}{f}\left[\left(\alpha_B + \frac{\alpha_X}{f}\right) + \pi g_L^B(\delta)\right]^{-1} + \pi g_L^A(\delta), \qquad [19a]$$

where $g_L^\varsigma(\delta)$ denotes the nondimensional Lorentzian line-shape function

$$g_L^\varsigma(\delta) = \frac{1}{\pi}\frac{\beta_\varsigma}{(\delta^2 + \beta_\varsigma^2)}, \quad \varsigma = \text{A, B}, \qquad [19b]$$

for the A- and B-spin components, respectively. We note, in [19a], that the rate $\alpha_A + \alpha_X$ represents the zeroth-order term when one assumes, as did Grad *et al.* (*15*), that the B spins are completely saturated and the RF is so far off resonance that it has no direct effect on the A spins. The next term corresponds to the correction when one relaxes the assumption on the saturation of the B spins. Thus far we have reproduced the results, in explicit fashion, of I. The last term corresponds to the direct effect of the RF on the A spins which was previously ignored.

The steady-state magnetization, $w_A(\infty)$, according to [12] is equal to $\xi(\infty)/\alpha_{app} = -(b + e)/\alpha_{app}$. By straightforward evaluation, one can verify that it regenerates the expression obtained by Wu (*16*). We shall not perform this exercise here. To complete the transient solution, we solve all the nonzero eigenvalues and eigenvectors of $q\mathbf{R}^T$ in Appendix C.

SOLUTIONS TO ON-RESONANCE BINOMIAL PULSED SATURATION

When the saturation RF is applied on resonance but with an amplitude modulated by a binomial function $\theta_1^n(\tau)$ (*17, 2*) where $\theta_1^n(\tau)$ is a uniamplitude, nth-order binomial function of the RF excitation, i.e., $\theta_1^n(\tau) \equiv \omega_1^n(\tau)/|\omega_1|$, where $n = 1, 2, \cdots$ specifies the amplitude modulation of $\theta_1^n(\tau)$ by the coefficients of x in the binomial expansions (1

$-x)^n$, one can also apply the P O technique to greatly simplify the analytical solution obtained in II. As we have shown previously in II, the solution under pulsed saturation must be divided into two regimes: the pulse-on regime and the free-induction regime when the saturation RF is turned off. The overall solution is obtained by solving the Bloch equations pertinent to each regime individually, using the end-of-period solution of one regime as the initial condition for the next regime and vice versa. The solution of the free-induction regime is simple and well known (*2-6*). Here we focus our effort to simplify the pulse-on solution obtained previously in II. During the period when the burst of RF pulses is turned on, the equations of motion according to the spin-bath model can be written in the same cardinal form as [5] with the vectors **X** and **Y** and the matrix **R** which have been modified as

$$\mathbf{X} = \mathrm{col}\{v_B, w_B, v_A, w_A\},$$

$$\mathbf{Y} = -\mathrm{col}\{\theta_1^n(\tau), 0, \theta_1^n(\tau), 0\} = -\theta_1^n(\tau)(\mathbf{e}_1 + \mathbf{e}_3) \quad [20a]$$

$$\mathbf{R} = \begin{bmatrix} \beta_B & -2\theta_1^n(\tau) & 0 & 0 \\ (1/2)\theta_1^n(\tau) & \alpha_B + \alpha_X/f & 0 & -\alpha_X/f \\ 0 & 0 & \beta_A & -2\theta_1^n(\tau) \\ 0 & -\alpha_X & (1/2)\theta_1^n(\tau) & \alpha_A + \alpha_X \end{bmatrix}. \quad [20b]$$

It should be noted that although $\theta_1^n(\tau)$ in Eq. [20] assumes the values +1 and −1 at different time intervals, it is constant during a particular phase of the pulse-on period.

To solve the transient problem, one needs to find the eigenvalues and eigenvectors of $q\mathbf{R}^T$ with the projection operator p now defined as $\mathbf{e}_4\mathbf{e}_4^T$. As is shown in Appendices A–C, the eigenvalues and their corresponding eigenvectors are readily found to be

$$\lambda_0 = 0, \quad \mathbf{v}_r^0 = \mathrm{col}\left\{-\frac{1}{2D}\theta_1^n(\tau)\alpha_X\beta_A, \frac{\alpha_X\beta_A\beta_B}{D}, -\frac{\theta_1^n(\tau)}{2\beta_A}, 1\right\},$$

$$\mathbf{v}_l^0 = \mathbf{e}_4^T, \quad [21a]$$

$$\lambda_1 = \beta_A, \quad \mathbf{v}_r^1 = \mathbf{e}_3, \quad \mathbf{v}_l^1 = \mathbf{e}_3^T + \frac{\theta_1^n(\tau)}{2\beta_A}\mathbf{e}_4^T, \quad [21b]$$

$$\lambda_\pm = \frac{1}{2}\left[\alpha_B + \frac{\alpha_X}{f} + \beta_B \pm \sqrt{\left(\alpha_B + \frac{\alpha_X}{f} - \beta_B\right)^2 - 4}\right],$$

$$\mathbf{v}_r^\pm = N_\pm \mathrm{col}\{\theta_1^n(\tau), -2(\beta_B - \lambda_\pm), 0, 0\},$$

$$\mathbf{v}_l^\pm = N'_\pm\,\mathrm{row}\left\{\theta_1^n(\tau), \frac{1}{2}(\beta_B - \lambda_\pm), 0, \frac{\alpha_X(\beta_B - \lambda_\pm)}{2\lambda_\pm}\right\}, \quad [21c]$$

where

$$D = \beta_A\left[\beta_B\left(\alpha_B + \frac{\alpha_X}{f}\right) + 1\right], \quad [21d]$$

and the normalization constants N and N' are related by

$$N_\pm N'_\pm\{1 - (\beta_B - \lambda_\pm)^2\} = 1.$$

The eigenvalues λ_1, λ_+, and λ_- are time constants of the transient components that may have contributions in $\varphi(\tau)$ and $\xi(\tau)$. For the spin-bath parameters of most systems of biological interest and a time scale of 1 ms (which is shorter than the typical pulse width one normally uses in this type of applications), $\lambda_1\tau \sim 0.01$ as compared to $\lambda_-\tau \sim 1$ and $\lambda_+\tau \sim 15$. Thus, for all practical purpose, we can ignore the contributions of the transients due to λ_+. We will show later that one can also ignore the contributions due to λ_-.

We first evaluate the production term $\xi(\tau)$, using the eigenvalues and eigenvectors given above. The asymptotic solution of this term $\xi_A(\infty)$ can be shown from Appendix B to be given by

$$\xi_A(\infty) = \mathbf{v}_r^{0T} \cdot \mathbf{Y} = -\mathbf{v}_r^{0T} \cdot (\mathbf{e}_1 + \mathbf{e}_3).$$

This implies that

$$\xi_A(\infty) = \frac{1}{2}\left(\frac{\alpha_X\beta_A}{D} + \frac{1}{\beta_A}\right), \quad [22]$$

which is independent of the initial conditions of the spin system. The expression for $\xi_A(\tau)$, however, depends on the initial condition $\mathbf{X}_q(0)$, and from the development leading to [B5], we can write

$$\xi(\tau) = \xi_A(\infty) - \sum_{j=1}^{3} e^{-\lambda_j\tau}(\mathbf{v}_l^j \cdot \mathbf{e}_4)\{\lambda_j\mathbf{v}_r^{jT} \cdot \mathbf{X}_q(0) + \mathbf{v}_r^{jT} \cdot \theta_1^n(\tau)(\mathbf{e}_1 + \mathbf{e}_3)\}.$$

Here we make a simplifying approximation using the fact that T_{2B} is so short that it is justified to consider v_B practically negligible at all times. So $\mathbf{X}_q(0) = \{0, w_B(0), v_A(0), 0\}$, which gives

$$\xi(\tau) = \xi[\tau, v_A(0), w_B(0)] = C_0 + C_1e^{-\beta_A\tau} + C_-e^{-\lambda_-\tau} + C_+e^{-\lambda_+\tau} \quad [23a]$$

with

$$C_0 = \xi_A(\infty) \quad [23b]$$

$$C_1 = -\frac{\theta}{2\beta_A}\{\beta_A v_A(0) + \theta\} \quad [23c]$$

$$C_\pm = \frac{\alpha_X(\beta_B - \lambda_\pm)[(\beta_B - \lambda_\pm)\omega_B(0) - 1/(2\lambda_\pm)]}{1 - (\beta_B - \lambda_\pm)^2}, \quad [23d]$$

where we have used the shorthand notation θ for $\theta_1^n(\tau)$. To solve the transient problem under the binomial pulse, we consider a solution of [9a] in the Laplace domain,

$$\tilde{w}_A(s) = [s + \alpha_0 + \tilde{\varphi}(s)]^{-1}[\tilde{\xi}(s) + w_A(0)] = G(s)[\tilde{\xi}(s) + w_A(0)], \quad [24a]$$

where

$$G(s) = \frac{1}{s + \alpha_0^A + \tilde{\varphi}(s)}, \quad \alpha_0^A = \alpha_A + \alpha_X. \quad [24b]$$

$G(s)$ and $\tilde{\xi}(s)$ are, respectively, the propagator and the source term that govern the time development of $w_A(\tau)$ from the initial state $w_A(0)$. If G and ξ change after a time period τ_1, as one would expect in the case of a binomial pulse, the time evolution of $w_A(\tau)$ in the Laplace domain can be obtained from [24a],

$$\tilde{w}_A(s) = G_1(s)[\tilde{\xi}_1(s) + w_A(\tau_1)],$$

where G_1 and $\tilde{\xi}_1$ are the new propagator and source, respectively. In general, after m such periods, the Laplace transform of the time evolution $w_A(\tau)$, $\tau > \sum_{j=1}^{m} \tau_j$, can be written as

$$\tilde{w}_A^m(s) = G_m(s)[\tilde{\xi}_m(s) + w_A(\tau_m)]. \quad [25]$$

To obtain $w_A(\tau)$, one needs to evaluate G and $\tilde{\xi}$ in every period of the pulse sequence. Now recall that G is given by [24b], which is dependent upon $\tilde{\varphi}(s)$. On the other hand, $\tilde{\varphi}(s)$ itself, according to a development similar to [B3] in Appendix B, is derived from a scalar product determined by the evolution of the quantity $\dot{\phi}(\tau)$:

$$\tilde{\varphi}(s) = -\sum_{j=1}^{3} \frac{\lambda_j}{s + \lambda_j}(\mathbf{v}_1^j \cdot \mathbf{e}_4)(\mathbf{v}_r^{j\mathrm{T}} \cdot q\mathbf{Re}_4) = \left(\frac{1}{s + \beta_A} - \frac{c_+}{s + \lambda_+} - \frac{c_-}{s + \lambda_-}\right) \quad [26a]$$

with

$$c_\pm = \frac{\alpha_X^2(\beta_B - \lambda_\pm)^2}{f\{1 - (\beta_B - \lambda_\pm)^2\}}. \quad [26b]$$

Thus far, the development is generally applicable to any amplitude- and phase-modulated RF pulses. From here on, we drop all transient contributions arising from λ_+ and λ_- on the grounds that both of the coefficients associated with these terms $C_\pm$ and $c_\pm$ as defined in Eqs. [23d] and [26b] are small in comparison with those of the other eigenvalues. For a detailed evaluation, we concentrate on the simplest form of the binomial pulses: the phase-alternated or the 1 $\bar{1}$ pulse sequence, which corresponds to the case when the index n in the amplitude-modulation function $\theta_1^n(\tau)$ is equal to 1. If the total pulse duration for each cycle of this pulse sequence is τ_w, then the response after one such cycle is obtained from repeated applications of the inverse Laplace transform of [25] evaluated at $\tau_1 = \frac{1}{2}\tau_w$ and $\tau = \tau_w$, respectively, with the propagators G and G_1 and the sources $\tilde{\xi}$ and $\tilde{\xi}_1$ evaluated according to Eqs. [24b], [26a], and [23a]. Ignoring terms in [26a] that give rises to the fast transients as just mentioned, we have

$$G = G_1 = \frac{1}{s + \alpha_0^A + 1/(s + \beta_A)} = \frac{s + \beta_A}{(s + \alpha_0^A)(s + \beta_A) + 1} \quad [27]$$

$$\tilde{\xi}(\theta, s) = \frac{1}{2s}\left(\frac{1}{\beta_A} + \frac{\alpha_X\beta_A}{D}\right) - \frac{1 + \theta\beta_A v_A(0)}{2\beta_A(s + \beta_A)} = \frac{\mu_A}{2s\beta_A} - \frac{1 + \theta\beta_A v_A(0)}{2\beta_A(s + \beta_A)} \quad [28a]$$

$$\mu_A = 1 + \frac{\alpha_X\beta_A}{1 + \beta_B\alpha_{0B}}, \quad \alpha_0^B = \alpha_B + \frac{\alpha_X}{f}. \quad [28b]$$

Substituting the above quantities into [25], one has, after rearrangement of terms,

$$\tilde{w}_A(s) = \frac{s + \beta_A}{(s + \alpha_0^A)(s + \beta_A) + 1} \times \left\{\frac{\mu_A}{2s\beta_A} - \frac{1 + \theta\beta_A v_A(0)}{2\beta_A(s + \beta_A)} + w_A(0)\right\}. \quad [29]$$

The time evolution $w_A(\tau)$ is the inverse Laplace transform of $\tilde{w}_A(s)$, which can be shown to be

$$w_A(\tau) = w_A(0)\left[\frac{\rho_A - \beta_A}{\sigma_A}\sinh(\sigma_A\tau) + \cosh(\sigma_A\tau)\right]e^{-\rho_A\tau} + \left[\left\{\gamma_A - \frac{\theta v_A(0)}{2\sigma_A}\right\}\sinh(\sigma_A\tau) - \kappa_A\left\{\frac{\rho_A}{\sigma_A}\sinh(\sigma_A\tau) + \cosh(\sigma_A\tau)\right\}\right]e^{-\rho_A\tau} + \kappa_A, \quad [30a]$$

where

$$\rho_A = \frac{1}{2}(\alpha_0^A + \beta_A), \quad \sigma_A = \sqrt{\left[\frac{(\alpha_0^A - \beta_A)}{2}\right]^2 - 1} \quad [30b]$$

$$\gamma_A = \frac{\mu_A - 1}{2\sigma_A\beta_A}, \quad \kappa_A = \frac{\mu_A}{2(\alpha_0^A\beta_A + 1)}. \quad [30c]$$

An expression similar to [30a] may be derived for $w_B(\tau)$ with the subscript A replaced everywhere by B with ρ_B, σ_B, γ_B, μ_B, and κ_B defined similarly as in [30b], [30c]. For the strength of the saturation RF fields typically used in our experiments, $\beta_B > 1 > \beta_A$, note that σ_A is usually imaginary while σ_B is real. Note also that in Eq. [30a], the corresponding term containing $v_A(0)$, in the case of the B spins, can be dropped since, as discussed earlier, $v_B(0)$ can be neglected in view of the short T_{2B} relaxation time. This is the sole reason why binomial pulses can achieve selective saturation of the B spins.

Since σ_A is larger than α_0^A, β_A, and ρ_A by two or three orders of magnitude, Eq. [30a] can be further approximated by

$$w_A(\tau) = w_A(0)\cosh(\sigma_A\tau)e^{-\rho_A\tau} + \left[\left\{\gamma_A - \frac{\theta v_A(0)}{2\sigma_A}\right\}\sinh(\sigma_A\tau) - \kappa_A\cosh(\sigma_A\tau)\right]e^{-\rho_A\tau} + \kappa_A. \quad [31]$$

For a time τ from the beginning to the end of a 1 $\tilde{1}$ binomial pulse, one can write

$$w_A(\tau) = w_A(0)\cosh(\sigma_A\tau)e^{-\rho_A\tau} + \left[\left\{\gamma_A - \frac{v_A(0)}{2\sigma_A}\right\}\sinh(\sigma_A\tau) - \kappa_A\cosh(\sigma_A\tau)\right]e^{-\rho_A\tau} + \kappa_A \quad \text{for } \tau \le \frac{1}{2}\tau_w, \quad [32a]$$

$$\begin{aligned} w_A(\tau) = {} & w_A(0)\cosh\left(\frac{\sigma_A\tau_w}{2}\right)\cosh\left\{\sigma_A\left(\tau - \frac{\tau_w}{2}\right)\right\}e^{-\rho_A\tau} \\ & + \left[\left\{\gamma_A - \frac{v_A(0)}{2\sigma_A}\right\}\sinh\left(\frac{\sigma_A\tau_w}{2}\right) - \kappa_A\cosh\left(\frac{\sigma_A\tau_w}{2}\right)\right] \\ & \times \cosh\left[\sigma_A\left(\tau - \frac{\tau_w}{2}\right)\right]e^{-\rho_A\tau} - \left\{\gamma_A + \frac{v_A(\tau_w/2)}{2\sigma_A}\right\} \\ & \times \sinh\left\{\sigma_A\left(\tau - \frac{\tau_w}{2}\right)\right\}e^{-\rho_A(\tau-\tau_w/2)} + \kappa_A \quad \text{for } \frac{\tau_w}{2} < \tau \leqslant \tau_w. \quad [32b] \end{aligned}$$

In Eq. [32], one needs also to evaluate the "initial" transverse magnetization v_A at various time points, which can be readily shown, by ignoring all longitudinal relaxation effect during the pulse, to be

$$v_A(\tau) = e^{-\rho_A\tau}\left(\cosh(\sigma_A\tau) + \frac{2\sigma_A}{4-\beta_A^2}\sinh(\sigma_A\tau)\{\beta_A v_A(0) + 2\theta[1 - 2w_A(0)]\}\right) \quad [33]$$

COMPARISON WITH SOLUTIONS BY THE LAPLACE TRANSFORM FOR HEAT-DENATURED ALBUMIN

The model parameters developed in I and II for heat-denatured albumin, in part by ancillary empirical determinations and in part by physical reasoning, were used again here for all the computations with no further adjustment. In addition, since in our formulations here we have included the contribution from the on- and near-resonance saturation of the free-water component, we need the parameter T_{2A} which can be readily measured to be approximately 80 ms.

In the case of pulsed saturation, results (not shown here in the interest of conciseness) were obtained using Eqs. [30]–[33] nearly identical to those presented in II, which is to be expected since both methods are nearly exact solutions to the same set of equations. However, in the case of continuous saturation, there are significant differences, particularly at low-frequency offsets, between the results reported in I and those obtained here. To illustrate these differences, typical results of apparent relaxation rate and steady-state magnetization as a function of the frequency offset of the saturation RF obtained by these two methods are shown in Fig. 1. There are two sources that contribute to these discrepancies. At low-frequency offsets, the difference is due to the fact that the solutions in I were obtained from a truncated set of coupled equations and consequently the effect of direct saturation of the A spins was not properly accounted for. At high-frequency offsets, there is also a small deviation in the apparent relaxation rate as shown in Fig. 1a. This results from the asymptotic solution used in the PO technique, which overestimates α_{app} at high-frequency offsets by an amount which can be shown to be on the order of $O(\alpha_B + \alpha_X/f)^{-2}$. While the difference is quite small under normal conditions, improved approximations for the "memory function," φ, could reduce this discrepancy. Finally, Fig. 2 shows the apparent longitudinal relaxation rates (Fig. 2a) and the steady-state magnetization M_z (Fig. 2b) as a function of the saturation RF amplitude at frequency offsets of 5 and 7.5 kHz, respectively. From the plots shown in Fig. 1 and Fig. 2, it is not difficult to conclude that for spin systems typified by heat-denatured albumin, the most efficient RF irradiations for solid spin saturation are those with an offset in the range of 5 to 10 kHz and an amplitude that gives a nutational frequency of 1000–2000 rad/s.

APPENDIX A

We start with

$$\left(\frac{d}{dx} + \mathbf{R}\right)\mathbf{X} = \mathbf{Y}. \quad [A1]$$

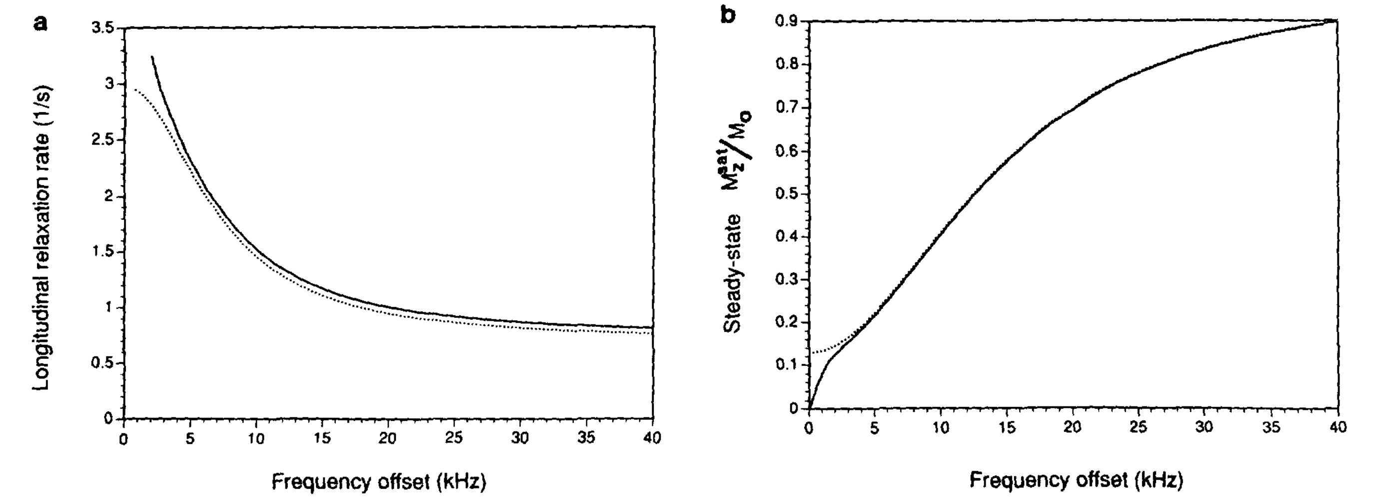

FIG. 1. Plots of calculated (a) apparent longitudinal relaxation rate and (b) steady-state longitudinal magnetization of heat-denatured albumin as a function of frequency offset of the saturation RF (ω_1 is fixed at 2026 rad/s) using previously obtained spin-bath parameters from Ref. (1). Solid line, solution, by the projection-operator technique, of a full set of coupled Bloch equations; broken line, solution, by the Laplace transform [Ref. (1)], of a truncated set of coupled Bloch equations.

Let

$$\mathbf{X}_p = p\mathbf{X}, \quad \mathbf{X}_q = q\mathbf{X} \qquad [A2]$$

$$\mathbf{Y}_p = p\mathbf{Y}, \quad \mathbf{Y}_q = q\mathbf{Y}. \qquad [A3]$$

Now note that since $\mathbf{Y} = -\mathbf{e}_2 - \mathbf{e}_5$, $p\mathbf{Y} = \mathbf{0}$ and $q\mathbf{Y} = \mathbf{Y}$, so that we have the decomposition

$$\frac{d}{d\tau}\mathbf{X}_p + p\mathbf{R}(\mathbf{X}_p + \mathbf{X}_q) = \mathbf{0} \qquad [A4]$$

$$\frac{d}{d\tau}\mathbf{X}_q + q\mathbf{R}(\mathbf{X}_p + \mathbf{X}_q) = \mathbf{Y}_q = \mathbf{Y}. \qquad [A5]$$

Solving [A5],

$$\mathbf{X}_q(\tau) = e^{-\tau q\mathbf{R}}\mathbf{X}_q(0) + \int_0^\tau ds e^{-(\tau+s)q\mathbf{R}}(\mathbf{Y} - q\mathbf{R}\mathbf{X}_p), \qquad [A6]$$

which implies that

$$\frac{d}{d\tau}\mathbf{X}_p + p\mathbf{R}\Big[\mathbf{X}_p + e^{-\tau q\mathbf{R}}\mathbf{X}_q(0) + \int_0^\tau ds e^{-(\tau-s)q\mathbf{R}}(\mathbf{Y} - q\mathbf{R}\mathbf{X}_p)\Big) = \mathbf{0}$$

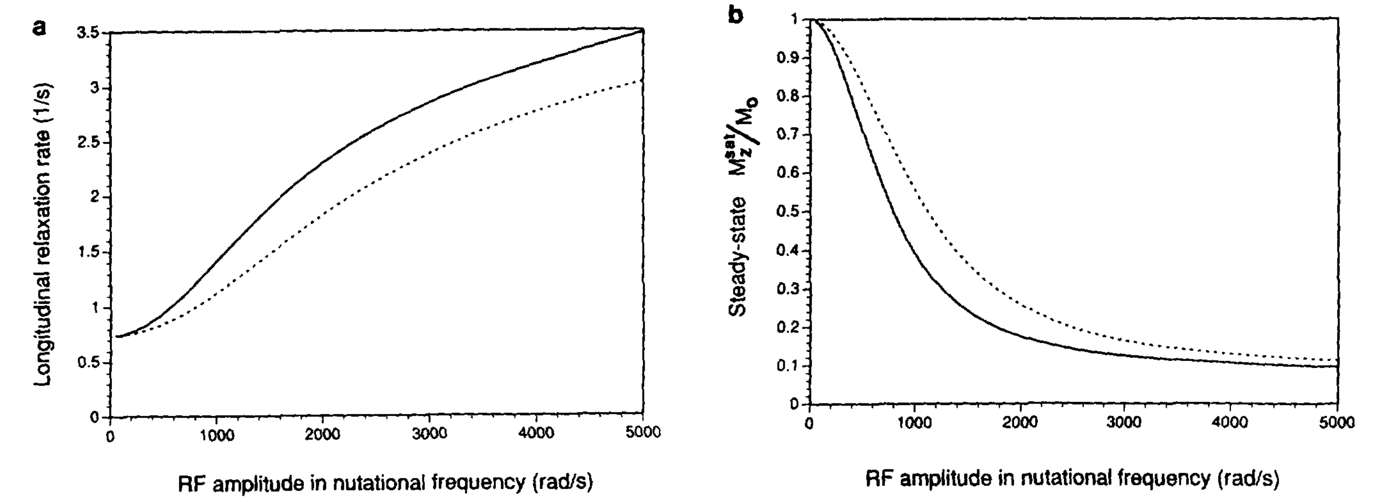

FIG. 2. Plots of calculated (a) apparent longitudinal relaxation rate and (b) steady-state longitudinal magnetization of heat-denatured albumin as a ınction of saturation RF amplitude using the projection-operator technique and spin-bath parameters obtained from Ref. (1). Solid line, frequency offset 5 kHz; broken line, frequency offset = 7.5 kHz.

or

$$\frac{d}{d\tau}\mathbf{X}_p + p\mathbf{R}\left[\mathbf{X}_p - \int_0^\tau dse^{-(\tau-s)q\mathbf{R}}q\mathbf{R}\mathbf{X}_p\right] = -p\mathbf{R}\left[\int_0^\tau dse^{-(\tau-s)q\mathbf{R}}\mathbf{Y} + e^{-\tau q\mathbf{R}}\mathbf{X}_q(0)\right]. \quad [A7]$$

Now we employ the initial condition $u(0) = v(0) = 0$, $w_\zeta = \eta_\zeta$, $\zeta = \mathrm{A, B}$, and hence $\mathbf{X}_q(0) = \mathrm{col}\{0, 0, \eta_\mathrm{B}, 0, 0, 0\} = \eta_\mathrm{B}\mathbf{e}_3$. Furthermore, since $\mathbf{X}_\mathrm{p}\cdot\mathbf{e}_6 = w_\mathrm{A}$, we form a scalar product of this expression with $\mathbf{e}_6^T$; then [A7] becomes

$$\frac{d}{d\tau}w_\mathrm{A} + (e_6^T\mathbf{R}\mathbf{e}_6)w_\mathrm{A} - \left[\int_0^\tau dsw_\mathrm{A}(s)(\mathbf{e}_6^T\mathbf{R}e^{-(\tau-s)q\mathbf{R}})q\mathbf{R}\mathbf{e}_6\right] = -\left[\int_0^\tau ds\mathbf{e}_6^T\mathbf{R}e^{-(\tau-s)q\mathbf{R}}\mathbf{Y} + \mathbf{e}_6^T\mathbf{R}e^{-\tau q\mathbf{R}}\mathbf{X}_q(0)\right]. \quad [A8]$$

Now consider a product of the form

$$(*) = [\mathbf{a}^T\mathbf{R}(q\mathbf{R})^m\mathbf{b}] = [\{\mathbf{R}^T\mathbf{a}\}^T(q\mathbf{R})^m\mathbf{b}] = [\{q\mathbf{R}^T\mathbf{a}\}^T\mathbf{R}(q\mathbf{R})^{m-1}\mathbf{b}],$$

m being an integer >1, since $q^T = q$. Following $m-1$ iterations,

$$(*) = (\{[q\mathbf{R}^T)^m\mathbf{a}\}^T\mathbf{R}\mathbf{b}) = (\{[q\mathbf{R}^T]^m\mathbf{a}\}^Tq\mathbf{R}\mathbf{b})$$

since q is idempotent, or $q^2 = q$, and therefore

$$(\mathbf{e}_6^T\mathbf{R}e^{-\tau q\mathbf{R}}q\mathbf{R}\mathbf{e}_6) = (\{q\mathbf{R}^Te^{-\tau q\mathbf{R}^T}\mathbf{e}_6\}^Tq\mathbf{R}\mathbf{e}_6).$$

We now define a new vector

$$\phi(\tau) \equiv e^{-\tau q\mathbf{R}^T}\mathbf{e}_6, \quad \dot\phi(\tau) = -q\mathbf{R}^Te^{-\tau q\mathbf{R}^T}\mathbf{e}_6; \quad [A9a]$$

then

$$(\mathbf{e}_6^T\mathbf{R}e^{-\tau q\mathbf{R}}q\mathbf{R}\mathbf{e}_6) = -[\dot\phi^T(\tau)\cdot q\mathbf{R}\mathbf{e}_6]. \quad [A9b]$$

We likewise have

$$-[\mathbf{e}_6^T\mathbf{R}e^{-\tau q\mathbf{R}}\mathbf{X}_q(0)] = \eta_\mathrm{B}[\dot\phi^T(\tau)\cdot\mathbf{e}_3] \quad [A10]$$

$$-(e_6^T\mathbf{R}e^{-\tau q\mathbf{R}}\mathbf{Y}) = [\dot\phi^T(\tau)\cdot\mathbf{Y}] = -[\dot\phi^T(\tau)\cdot(\mathbf{e}_2+\mathbf{e}_5)]. \quad [A11]$$

By using [A9] to [A11], [A8] can be rewritten as

$$\frac{d}{d\tau}w_\mathrm{A} + R_{66}w_\mathrm{A} + \left(\int_0^\tau ds\varphi(\tau-s)w_\mathrm{A}(s)\right) = \xi(\tau), \quad [A12]$$

where

$$\varphi(\tau) \equiv [\dot\phi^T(\tau)\cdot(q\mathbf{R})\mathbf{e}_6] \quad [A13]$$

$$\xi(\tau) \equiv [\dot\phi^T(\tau)\cdot\mathbf{X}_q(0)] + \int_0^\tau ds\dot\phi^T(\tau-s)\cdot\mathbf{Y}. \quad [A14]$$

APPENDIX B

Let $\mathbf{v}_1^j$, $\mathbf{v}_r^j$ denote left and right eigenvectors of the operator $q\mathbf{R}^T$, respectively. Since $\mathbf{e}_6^Tq\mathbf{R}^T = 0$, there is at least one zero eigenvalue with $\mathbf{v}_1^0 = \mathbf{e}_6^T$ its left eigenvector and, in this case, five more nonzero eigenvalues. Let us number these by the indices $j = 0, 1, 2, 3, 4, 5$. Applying the identity operator $\mathbf{1} \equiv (\sum_{j=0}^5 \mathbf{v}_r^j\mathbf{v}_1^j)$ to [A9], we obtain

$$\phi(\tau) = e^{-\tau q\mathbf{R}^T}(\sum_{j=0}^5 \mathbf{v}_r^j\mathbf{v}_1^j)\cdot\mathbf{e}_6 = (\mathbf{v}_1^0\cdot\mathbf{e}_6)\mathbf{v}_r^0 + \sum_{j=1}^5 e^{-\lambda_j\tau}(\mathbf{v}_1^j\cdot\mathbf{e}_6)v_r^j \quad [B1]$$

$$\dot\phi(\tau) = -\sum_{j=1}^5 \lambda_je^{-\lambda_j\tau}\mathbf{v}_r^j(\mathbf{v}_1^j\cdot\mathbf{e}_6), \quad [B2]$$

where we have used the relation $q\mathbf{R}^T\mathbf{v}_r^j = \lambda_j\mathbf{v}_r^j$. Therefore, from [A13],

$$\varphi(\tau) \equiv [\dot\phi^T(\tau)\cdot q\mathbf{R}\mathbf{e}_6] = -\sum_{j=1}^5 \lambda_je^{-\lambda_j\tau}(\mathbf{v}_1^j\cdot\mathbf{e}_6)(\mathbf{v}_r^{jT}\cdot q\mathbf{R}\mathbf{e}_6). \quad [B3]$$

Now making use of the condition $\mathbf{Y} = -\mathbf{e}_2 - \mathbf{e}_5$, $\mathbf{X}_q(0) = \eta_\mathrm{B}\mathbf{e}_3$, we have from [A14]

$$\xi(\tau) \equiv \dot\phi^T(\tau)\cdot\mathbf{X}_q(0) + \int_0^\tau \dot\phi^T(\tau-s)\cdot\mathbf{Y}ds = -\eta_\mathrm{B}\sum_{j=1}^5 \lambda_j\mathbf{e}^{-\lambda_j\tau}(\mathbf{v}_1^j\cdot\mathbf{e}_6)(\mathbf{v}_r^{jT}\mathbf{e}_3) + \sum_{j=1}^5 \lambda_j\int_0^\tau ds^{-\lambda_j(\tau-s)}(\mathbf{v}_1^j\mathbf{e}_6)\{\mathbf{v}_r^{jT}(\mathbf{e}_2+\mathbf{e}_5)\}.$$

But $\lambda_j\int_0^\tau dse^{-\lambda_j(\tau-s)} \equiv 1 - e^{-\tau\lambda_j}$, which implies that

$$\xi(\tau) = \sum_{j=1}^5 (\mathbf{v}_1^j\cdot\mathbf{e}_6)\{\mathbf{v}_r^{jT}\cdot(\mathbf{e}_2+\mathbf{e}_5) - \sum_{j=1}^5 e^{-\lambda_j(\tau-s)}(\mathbf{v}_1^j\cdot\mathbf{e}_6) \times\{\lambda_j\mathbf{v}_r^{jT}\cdot(\eta_\mathrm{B}\mathbf{e}_3 + \mathbf{v}_r^{jT}\cdot(\mathbf{e}_2+\mathbf{e}_5)\}. \quad [B4$$

Finally, we use $\sum_{j=1}^5 \mathbf{v}_1^j\mathbf{v}_r^j \equiv \mathbf{1} - \mathbf{v}_r^0\mathbf{v}_1^0$ to write, for any vecto $\mathbf{V}$ that is orthogonal to $\mathbf{e}_6$

$$\sum_{j=1}^{5} (\mathbf{v}_1^j \mathbf{e}_6)\{\mathbf{v}_r^{jT}\mathbf{V}\} = \sum_{j=1}^{5} \{\mathbf{V}^T \cdot \mathbf{v}_r^j \mathbf{v}_1^j \cdot \mathbf{e}_6\}$$
$$= -(\mathbf{V}^T \cdot \mathbf{v}_r^0 \mathbf{v}_1^0 \cdot \mathbf{e}_6) = -(\mathbf{V}^T \cdot \mathbf{v}_r^0),$$

which leads to

$$\xi(\tau) = -(\mathbf{e}_2 + \mathbf{e}_5)^T \cdot \mathbf{v}_r^0\}$$
$$- \sum_{j=1}^{5} e^{-\lambda_j \tau}(\mathbf{v}_1^j \cdot \mathbf{e}_6)\{\lambda_j \mathbf{v}_r^{jT} \cdot \eta_B \mathbf{e}_3 + \mathbf{v}_r^{jT} \cdot (\mathbf{e}_2 + \mathbf{e}_5)\}. \quad [B5]$$

Asymptotically, it is clear that as $\tau \rightarrow \infty$,

$$\xi(\tau) \rightarrow \xi(\infty) = -(\mathbf{e}_2 + \mathbf{e}_5)^T \cdot \mathbf{v}_r^0, \quad [B6]$$

and the memory term in the equation of motion for $w_A \rightarrow \int_0^\infty ds\varphi(s)$:

$$\int_0^\infty ds\varphi(s) = -\sum_{j=1}^{5} \lambda_j \int_0^\infty ds e^{-\lambda_j s}(\mathbf{v}_1^j \cdot \mathbf{e}_6)\{\mathbf{v}_r^{jT} \cdot q\mathbf{R}\mathbf{e}_6)$$
$$= -\sum_{j=1}^{5} (\mathbf{v}_1^j \cdot \mathbf{e}_6)\{\mathbf{v}_r^{jT} \cdot q\mathbf{R}\mathbf{e}_6)$$
$$= -(q\mathbf{R}\mathbf{e}_6)^T \sum_{j=1}^{5} \mathbf{v}_r^j \mathbf{v}_1^j \cdot \mathbf{e}_6$$
$$= -(q\mathbf{R}\mathbf{e}_6)^T(\mathbf{1} - \mathbf{v}_r^0 \mathbf{v}_1^0) \cdot \mathbf{e}_6$$
$$= -(e_6^T \cdot q\mathbf{R}\mathbf{e}_6) + (\mathbf{v}_1^0 \cdot \mathbf{e}_6)(\mathbf{v}_r^{0T} \cdot q\mathbf{R}\mathbf{e}_6)$$

or

$$\int_0^\infty ds\varphi(s) = \mathbf{v}_r^{0T} \cdot q\mathbf{R}\mathbf{e}_6. \quad [B7]$$

APPENDIX C

The eigenvalues for $q\mathbf{R}^T$ are determined as solutions of the characteristic equation $\det|q\mathbf{R}^T - \lambda\mathbf{1}| = 0$. One root corresponds to $\lambda = 0$, and the remaining roots satisfy

$$\det\begin{bmatrix} \beta_B - \lambda & -\delta & 0 & 0 & 0 \\ \delta & \beta_B - \lambda & 1/2 & 0 & 0 \\ 0 & -2 & \alpha_B + \alpha_X/f - \lambda & 0 & 0 \\ 0 & 0 & 0 & \beta_A - \lambda & -\delta \\ 0 & 0 & 0 & \delta & \beta_A - \lambda \end{bmatrix} = 0. \quad [C1]$$

Since the matrix of the determinant is block diagonal, [C1] can be solved by inspection. Two of the eigenvalues can be obtained by solving the lower-right block:

$$\lambda_{4,5} = \beta_A \pm i\delta. \quad [C2]$$

The other three eigenvalues are the roots of the equation from the upper-left block:

$$(\beta_B - \lambda)[(\beta_B - \lambda)(\alpha_B + \alpha_X/f - \lambda) + 1]$$
$$+ \delta^2(\alpha_B + \alpha_X/f - \lambda) = 0. \quad [C3]$$

By setting $y = \beta_B - \lambda$, $\psi = \alpha_B + \alpha_X/f - \beta_B$, [C3] is recast into the form

$$y^3 + \psi y^2 + (\delta^2 + 1)y + \delta^2\psi = 0. \quad [C4]$$

This is further transformed into the standard form with a vanishing quadratic term, i.e., $x^3 + ax + b = 0$, by letting

$$y = x - \psi/3,$$

where

$$a = \tfrac{1}{3}[3(\delta^2 + 1) - \psi^2] \quad [C5]$$
$$b = \tfrac{1}{3}\psi[\tfrac{1}{9}\psi^2 + 2\delta^2 - 1]. \quad [C6]$$

with the roots then given in terms of

$$\lambda_{1,2,3} = A + B, \quad -\frac{b}{2}\{(A + B) \pm i\sqrt{3}(A - B)\}, \quad [C7]$$

$$A \equiv \left(-\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}\right)^{1/3} \quad [C8a]$$

$$B \equiv \left(-\frac{b}{2} - \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}\right)^{1/3}. \quad [C8b]$$

For the eigenvectors that have been determined already in the text, $\mathbf{v}_1^0 = \mathbf{e}_6^T$ and $\mathbf{v}_r^0 = \text{col}\{a, b, c, d, e, 1\}$, with the expressions for a to e given by [17]. In view of the block separability of the remaining eigenvalues, it should be possible to try a similar ansatz to determine the corresponding eigenvectors. Consider first the vectors for which $(\beta_A - \lambda)^2 + \delta^2 = 0$. Let us write $\mathbf{v}_r = \text{col}\{0, 0, 0, M, N, 0\}$, which implies that $(\beta_A - \lambda)M - \delta N = 0$ or $M = [\delta/(\beta_A - \lambda)]N$, with N to be determined by normalization. Likewise, let $\mathbf{v}_1 = \text{row}\{0, 0, 0, M', N', P'\}$, for which we find $(\beta_A = \lambda)M' - \delta N' = 0$ and $N'/2 - \lambda P' = 0$, or $M' = [-\delta/(\beta_A - \lambda)]N'$, $P' = N'/2\lambda$. In as much as N and N' are arbitrary, apart from a normalization requirement, we can choose $N = N'$ and apply the condition $v_1 v_r = 1$, which yields

$$N^2\left[-\frac{\delta^2}{(\beta_A - \lambda)^2} + 1\right] = 1;$$

but $-\delta^2/(\beta_A - \lambda)^2 = 1$, which means $N = 1/\sqrt{2}$. Therefore, we may choose

$$\mathbf{v}_r^\lambda = \frac{1}{\sqrt{2}} \operatorname{col}\left\{0, 0, 0, \frac{\delta}{(\beta_A - \lambda)}, 1, 0\right\} \qquad [C9a]$$

$$\mathbf{v}_l^\lambda = \frac{1}{\sqrt{2}} \operatorname{row}\left\{0, 0, 0, \frac{-\delta}{(\beta_A - \lambda)}, 1, \frac{1}{2\lambda}\right\} \qquad [C9b]$$

for λ satisfying $(\beta_A - \lambda)^2 + \delta^2 = 0$. The eigenvectors $\mathbf{v}_{l,r}^\lambda$ for λ satisfying [C3] can be calculated using similar arguments. For conciseness, we left out the details and simply provide the results as

$$\mathbf{v}_r^\lambda = N \operatorname{col}\left\{\frac{\delta}{(\beta_B - \lambda)}, 1, \frac{2}{(\alpha_B + \alpha_X/f - \lambda)}, 0, 0, 0\right\}$$

$$\mathbf{v}_l^\lambda = N' \operatorname{row}\left\{\frac{-\delta}{(\beta_A - \lambda)}, 1, \frac{-1}{2(\alpha_B + \alpha_X/f - \lambda)}, 0, 0, \frac{\alpha_X}{\lambda(\alpha_B + \alpha_X/f - \lambda)}\right\},$$

where N and N' are determined by normalization; i.e.,

$$1 = NN'\left\{1 - \frac{\delta^2}{(\beta_B - \lambda)^2} - \frac{1}{(\alpha_B + \alpha_X/f - \lambda)^2}\right\}.$$

But $[(\beta_B - \lambda)^2 + \delta^2](\alpha_B + \alpha_X/f - \lambda) = -(\beta_B - \lambda)$, which implies

$$1 = NN'\left\{1 - \frac{\delta^2 + [(\beta_B - \lambda)^2 + \delta^2]^2}{(\beta_B - \lambda)^2}\right\}.$$

So if we let

$$1 - \frac{\delta^2 + [(\beta_B - \lambda)^2 + \delta^2]^2}{(\beta_B - \lambda)^2} \equiv e^{i \arg(\eta)} |\eta|,$$

where arg denotes argument, then we may write

$$N = \sqrt{|\eta|}, \quad N' = e^{-i \arg(\eta)} \sqrt{|\eta|}.$$

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