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Use of computer algebra for the study of quadrupole spin systems

By D. J. ISBISTER†
Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6

MANGALA S. KRISHNAN‡
Département de chimie, Université de Montréal, C. P. 6128, Succursale A, Montreal, PQ, Canada H3C 3J7

and B. C. SANCTUARY
Department of Chemistry, McGill University, 801 Sherbrooke West, Montreal, PQ, Canada H3A 2K6

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Analytical computation of the effect of radiofrequency pulses and free evolution between pulses are studied in a spin system dominated by the nuclear electric quadrupole interaction using 'symbolic computer algebra'. The program MAPLE is used to compute spin density matrices for single spin systems with spin magnitude $I = 1, 3/2, 2$ and $5/2$. In all cases except $I = 5/2$, the pure nuclear electric quadrupole Hamiltonian with arbitrary asymmetry parameter η is used to obtain results for a single pulse and an evolution period following the pulse. In the spin 5/2 system η is set to zero. The calculations are done using a simple matrix representation of the density operator and the Baker–Campbell–Hausdorff formula. In addition, the validity of dropping non-secular (i.e., time-dependent) terms from the Hamiltonian for the pulse in the quadrupole interaction frame is examined for the spin 1 case using a truncated Magnus expansion.

1. Introduction

Pulses in both nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are generated by bursts of linearly polarized radiofrequency (RF) radiation. The magnetic component along a chosen direction ($\hat{x}$) is given by

$$\mathbf{H}(t) = 2\hat{x}H_1 \cos(\omega t - \phi), \tag{1}$$

where ω is the carrier frequency, H_1 the amplitude and ϕ the phase of the field. Time dependent field (1) can be broken up into two oppositely rotating components as

$$\mathbf{H}(t) = \mathbf{H}^+(t) + \mathbf{H}^-(t) \tag{2}$$

where

$$\mathbf{H}^+(t) = H_1[\hat{x}\cos(\omega t - \phi) - \hat{y}\sin(\omega t - \phi)] \tag{3}$$

and

$$\mathbf{H}^-(t) = H_1[\hat{x}\cos(\omega t - \phi) + \hat{y}\sin(\omega t - \phi)]. \tag{4}$$

† Permanent address: Department of Physics, University of NSW, University College, ADFA, Canberra, ACT 2600, Australia.

‡ Present address: Department of Chemistry, Queen's University, Kingston, Ontario Canada K7L 3N6.

NMR and NQR spectroscopy differ in a fundamental way due to:

the fact that the external magnetic field $H_0\hat{z}$ is dominating in the former and absent or very small in the latter; and
the approximation in neglecting one of the components of the time-dependent field [1] in the former or keeping both components of the rotating field and treating the evolution of spins as the net evolution due to two independent RF fields [2] in the latter.

In the presence of large static magnetic fields H_0 as is common in NMR, nuclear spins precess about the static field with the Larmor frequency ω_0 ($=\gamma H_0$ where γ is the gyromagnetic ratio). The neglect of one of the components [1] is therefore based on physical intuition: namely, the component rotating at twice the Larmor frequency in the opposite direction in a rotating frame of reference will have little effect in resonance absorption. Its inclusion as a perturbation correction does lead, however, to a small shift in the resonance frequency, known as the Bloch–Siegert shift [3].

In contrast, NQR spectroscopy deals with systems having a dominant energy level structure due to interaction between the electric quadrupole moment of the nucleus ($I \geqslant 1$) and the electric field gradients due to the non-spherical charge distribution outside the nucleus. There is no analogue of the Larmor frequency in pure NQR since quadrupole interactions result in more than one frequency for each spin magnitude (with the exception of spin 3/2). The effect of RF pulses in such systems was considered in [2]. The approach outlined in [2] is novel in that it describes the effect of pulses as causing transitions between pairs of levels by *both* $\mathbf{H}^+(t)$ (equation (3)) and $\mathbf{H}^-(t)$ (equation (4)) *and independently of each other*. Mathematically, it means that one *can* describe the effect of RF pulses by a set of uncoupled 2×2 matrices for quadrupole systems. In analogy with the treatment in NMR, non-secular terms were ignored, namely in describing the effect of $\mathrm{H}^+(t)$, terms arising due to 'out-of-phase' component $\mathbf{H}^-(t)$ were ignored, and vice versa. In this way, the effect of pulses in spin systems dominated by a quadrupole can be visualized physically. The results obtained are identical to those arrived at by a more elaborate and tedious procedure [4]. Moreover, subsequent work in NQR [5] has shown that the theory described in [2] can be used for composite pulses to reproduce results obtained previously by others [6].

The theory presented in [2] is not, however, comprehensive. Attention was restricted to the dominant part of the electric quadrupole Hamiltonian, namely the axially symmetric case ($\eta = 0$). Moreover, the neglect of non-secular terms was not investigated fully. Also, in the case of integer spins, transitions from the non-degenerate level ($M = 0$) to the nearby pair of degenerate levels ($M = \pm 1$) led to expressions which agree with those for the treatment of selective excitation in NMR but disagree with other work in NQR by a numerical factor in the effective pulse amplitude $\omega_{1,\mathrm{eff}}$. In the NMR case, the pulse for selective excitation from level $M = 0$ to level $M = 1$ in a spin 1 system has the RF amplitude, $\omega_1 = \gamma H_1$, increased by a well known factor $\sqrt{2}$ to give $\omega_{1,\mathrm{eff}} = \sqrt{2}\omega_1$ [7–9]. This is also known as the Rabi frequency. In [2] this result was obtained by using rotating and counter-rotating components as independent RF Hamiltonians for spin 1. This contrasts with the result for pure NQR for which $\omega_{1,\mathrm{eff}} = 2\omega_1$ [10] and is obtained by the direct use of expression (1) without the need to treat separately the circularly polarized fields $\mathbf{H}^+(t)$ and $\mathbf{H}^-(t)$. The discrepancy between the two results is due to the fact that the Hamiltonians $\mathbf{H}^+(t)$ and $\mathbf{H}^-(t)$ associated with the rotating and counter-rotating components of equation (1) do not commute only in the case of transitions from $M = 0$ to $M = \pm 1$ (for all integer spins). In NMR, only one component is retained, leading to the result $\omega_{1,\mathrm{eff}} = \sqrt{2}\omega_1$. In the NQR case, not only does one need to include both components of the RF field but also the effect of non-commutation between the two Hamiltonians. The latter was inadvertently omitted in [2] and needs to be corrected. This problem does not arise, however, in the treatment expounded in [2] for spin 3/2 or selective excitations not involving a single common level.

The motivation for this article arises, however, from the necessity to treat axially asymmetric ($\eta \neq 0$) quadrupole systems in a simple manner and to examine more closely the neglect of non-secular terms from the RF Hamiltonian expressed in the quadrupole interaction frame (QIF) [11]. It is also necessary to consider RF pulses in an arbitrary direction with respect to the principal axis frame. In the past, the solution of the spin density matrix for quadrupolar systems with $I = 1, 3/2$ has been obtained by the use of various quantum representations [7, 12–15]. Besides the well known $|IM\rangle$ basis, others such as the fictitious spin 1/2 [12, 13], multiplet spin [7], spherical tensor [14] and variations of it [4, 15] have been used. The axially symmetric case is quite simple to study in the $|IM\rangle$ basis for all spins, and considerably more tedious in all other bases mentioned above; the axially asymmetric case is best studied in the basis of eigenfunctions of the quadrupole Hamiltonian. The algebraic details are dependent to a large extent on the spin magnitude, and become more tedious and error prone with increasing magnitude of I. In this respect, matrix algebra for individual spins has a great physical appeal and is the simplest to follow. Because of the availability of reliable and powerful computer algebraic programs such as REDUCE [16], MATHEMATICA [17] and, more recently, MAPLE [18], it is indeed possible to follow the dynamics of spins subject to strong quadrupole interactions which hitherto were considered intractable. In particular, we employ MAPLE to treat a number of these problems. They include problems for spins with magnitudes $I = 1, 3/2, 2$ with $\eta \neq 0$ and $I = 5/2$ with $\eta = 0$. Moreover, we use MAPLE to investigate the validity of the neglect of non-secular terms from the RF Hamiltonian for the $I = 1$ system. A truncated Magnus expansion is used for this purpose. For all other cases, it is shown that the Baker–Campbell–Hausdorff formula is ideal for implementation by MAPLE. A segment of the MAPLE code used to compute the results described in this article is given in the Appendix. Here we examine only the effect of a single pulse followed by an evolution period in a matrix representation in which the quadrupole Hamiltonian is diagonal.

2. Basic theory

In the absence of external magnetic fields, the spin Hamiltonian for a quadrupolar nucleus is given by the quadrupole Hamiltonian $\mathbf{H}_\mathrm{Q}$ in the principal axis frame

$$\mathbf{H}_\mathrm{Q} = -\frac{\hbar e^2Qq}{4I(2I-1)}\left\{(I^2 - 3I_z^2) - \frac{\eta}{2}(I_+^2 + I_-^2)\right\} \equiv -\frac{\hbar e^2Qq}{4I(2I-1)} I_\mathrm{Q}(\eta), \qquad (5)$$

where e^2Qq is the quadrupole coupling constant and η the asymmetry parameter. For details see [19]. The effect of RF pulses is included by adding the RF Hamiltonian

$$\begin{aligned}\mathbf{H}_1(t) &= -2\hbar\gamma H_1 I_x \cos(\omega t - \phi) \\ &= -2\hbar\omega_1 I_x \cos(\omega t - \phi) \qquad (6)\end{aligned}$$

to give

$$\mathbf{H}(t) = \mathbf{H}_Q + \mathbf{H}_1(t). \tag{7}$$

The x component indicates that the pulse is applied along the x axis with respect to the principal axis frame. The time evolution of the spin system subject to equation (7) is often studied by following the evolution of the spin density operator in the interaction representation [1] with the quadrupole Hamiltonian as the appropriate zero-order Hamiltonian. Consequently, all operators in this representation are given by

$$\tilde{O}_{op} = \exp\left\{\frac{i\mathbf{H}_Q t}{\hbar}\right\} O_{op} \exp\left\{-\frac{i\mathbf{H}_Q t}{\hbar}\right\}. \tag{8}$$

In the high temperature approximation, the equilibrium spin density matrix differs from the quadrupole Hamiltonian by scalar factors alone. Its matrix representation is therefore diagonal in the basis of eigenfunctions of $\mathbf{H}_Q$. For $\eta = 0$ the $|IM\rangle$ basis is the natural choice for $\mathbf{H}_Q$, although other representations have been used in the past. For $\eta \neq 0$, we use the $|IM\rangle$ basis in the case of spins $I = 1$ and $I = 3/2$ and the eigenfunctions of the quadrupole Hamiltonian for spin $I = 2$. The algebra is simple in the $I = 1$ and $I = 3/2$ cases, and therefore the basis of eigenfunctions of the quadrupole Hamiltonian is not needed. However, for higher spin quantum numbers it is best to employ, whenever possible, the eigenfunctions of the quadrupole Hamiltonian. The RF Hamiltonian in the interaction frame is given as

$$\tilde{\mathbf{H}}_1(t) = \exp\left\{\frac{i\mathbf{H}_Q t}{\hbar}\right\} \mathbf{H}_1(t) \exp\left\{-\frac{i\mathbf{H}_Q t}{\hbar}\right\}, \tag{9}$$

and evaluated by the use of the well-known Baker–Campbell–Hausdorff (BCH) formula

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + \frac{1}{3!}[A, [A, [A, B]]] + \cdots. \tag{10}$$

The evaluation of equation (9) using (10) must be done separately for each spin magnitude I. This is to be contrasted with NMR, where the presence of a dominant static magnetic field enables one to define an interaction representation simply as

$$\tilde{O}_{op} = \exp\{i\omega_0 t I_z\} O_{op} \exp\{-i\omega_0 t I_z\}, \tag{11}$$

and evaluate all operators independently of the spin magnitude. The essential feature of computer-assisted algebra in the case of NQR is, therefore, the ease with which equation (9) can be evaluated using (10). The time evolution of the spin density matrix in the interaction representation due to the effective RF Hamiltonian is then given by

$$i\hbar \frac{\partial \tilde{\rho}}{\partial t} = [\tilde{\mathbf{H}}_1(t), \tilde{\rho}(t)]. \tag{12}$$

Retaining only the time-independent terms in the effective RF Hamiltonian near or at resonance, the solution of equation (12) is given approximately by

$$\tilde{\rho}(t) = \exp\left\{-\frac{i\tilde{\mathbf{H}}_1^* t}{\hbar}\right\} \tilde{\rho}(0) \exp\left\{\frac{i\tilde{\mathbf{H}}_1^* t}{\hbar}\right\}, \tag{13}$$

where $\tilde{\mathbf{H}}_1^*$ is the time-independent or secular part of $\tilde{\mathbf{H}}_1(t)$. Evaluation of equation (13) using (10) for various spin magnitudes is simplified by the use of MAPLE.

The expectation value of the operators I_x and I_y are computed easily by the trace relation

$$\langle I_i(t)\rangle = \mathrm{Tr}\,[I_i(t)\rho(t)] = \mathrm{Tr}\,[\tilde{I}_i(t)\tilde{\rho}(t)], \quad i = x, y. \tag{14}$$

In section 3, MAPLE is used to obtain results for spins 1 and 3/2 by dropping non-secular terms from the effective RF Hamiltonian. The results are previously well known and are included here to illustrate the ease with which the MAPLE program described in the Appendix can be used. In section 4 the time-dependent terms are included in the effective RF Hamiltonian for spin 1 to lowest order and the solution of equation (12) is given by employing a truncated Magnus expansion (also to lowest order) and MAPLE. When the carrier frequency is equal to the transition frequency, and when the time dependence of the effective RF field can be neglected, the solutions in section 4 reduce to those for spin 1 in section 3. In section 5 the RF Hamiltonian is split into rotating and counter-rotating components as in equations (2)–(4) and it is shown that for spin 1 the components yield forms which are in agreement with the NMR selective excitation case; the expressions differ, however, by virtue of the presence of common level $M = 0$, from the result obtained by retaining the RF field in the form of equation (1). In section 6, results are presented for the $I = 2$ case with $\eta \neq 0$. Section 7 employs MAPLE for spin 5/2 case where it is assumed that $\eta = 0$.

3. Secular Hamiltonian approach for pulses in the case of spins 1 and 3/2

In this section we consider a single spin system with $I = 1$ first. The RF Hamiltonian is not split into rotating/counter-rotating components but kept as in equation (1). It is evaluated in the interaction frame by using BCH expansion (10) for $\tilde{I}_x$ given by

$$\tilde{I}_x = \exp\{i\chi I_Q(\eta)\} I_x \exp\{-i\chi I_Q \eta)\}, \tag{15}$$

where $\chi = -(t\tilde{Q})/2$ and $\tilde{Q} = (e^2Qq)/2$. Using MAPLE it is a simple matter in this case to obtain the following expression for the effective RF Hamiltonian $\tilde{\mathbf{H}}_1(t)$ as

$$\tilde{\mathbf{H}}_1(t) = \left[\frac{i}{\sqrt{2}}\sin\left\{\frac{(\eta+3)\tilde{Q}t}{2}\right\}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + \frac{1}{\sqrt{2}}\cos\left\{\frac{(\eta+3)\tilde{Q}t}{2}\right\}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\right]$$
$$\times\,[-2\hbar\omega_1\cos(\omega t - \phi)]. \tag{16}$$

Combining the trigonometric functions and setting $\phi = 0$ for convenience, the secular contribution $\tilde{\mathbf{H}}_1^*$ is obtained,

$$\tilde{\mathbf{H}}_1^* = -\frac{\hbar\omega_1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = -\hbar\omega_1 I_x, \tag{17}$$

where ω in equation (16) has been set to $[(\eta + 3)\tilde{Q}t]/2$. The expression for $\tilde{\mathbf{H}}_1^*$ in equation (17) is independent of η, a result unique to the spin $I = 1$ case.

The thermal equilibrium density operator is given by

$$\tilde{\rho}(0) \propto \frac{\beta\hbar\tilde{Q}}{2} I_Q(\eta), \tag{18}$$

after omitting the identity operator and a normalization factor. Assuming that the secular approximation $\tilde{\mathbf{H}}_1^*$ to $\tilde{\mathbf{H}}_1(t)$ is sufficient, MAPLE is used to obtain the time-dependence of $\tilde{\rho}(t_1^p)$ given by equation (13) where t_1^p is the duration of the RF field. $\tilde{\rho}(0)$ is expressed in the $|IM\rangle$ basis. Resolution of the nested commutators leads to the following expression for $\tilde{\rho}(t_1^p)$, namely

$$\tilde{\rho}(t_1^p) \propto \frac{\beta\hbar\tilde{Q}}{2}\left[I_Q(\eta) + \frac{i(3+\eta)}{\sqrt{8}} \sin(2\omega_1 t_1^p) \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + \frac{\eta+3}{4}\{\cos(2\omega_1 t_1^p) - 1\} \begin{pmatrix} -1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & -1 \end{pmatrix}\right]. \tag{19}$$

By virtue of the interaction representation, it follows that

$$\tilde{\rho}(t_1^p) = \tilde{\rho}(t_1^p + t_1), \tag{20}$$

where t_1 is the time for which the spin system evolves following a pulse in the absence of other static interactions. The density operator $\tilde{\rho}(t_1^p + t_1)$ may be used to define the initial condition for subsequent pulses. On the other hand, the expectation value of any operator A can be calculated as

$$\langle A\rangle(t_1^p + t_1) = \mathrm{Tr}\,\{\tilde{\rho}(t_1^p + t_1)\tilde{A}(t_1^p + t_1)\}, \tag{21}$$

where

$$\tilde{A}(t_1^p + t_1) = \exp\left\{\frac{i\mathbf{H}_Q(t_1^p + t_1)}{\hbar}\right\} A \exp\left\{-\frac{i\mathbf{H}_Q(t_1^p + t_1)}{\hbar}\right\}. \tag{22}$$

We then find that

$$\langle I_x\rangle(t_1 + t_1^p) \propto \tfrac{1}{2}\beta\hbar\tilde{Q}(\eta+3)\sin(2\omega_1 t_1^p)\sin\left\{\frac{(\eta+3)\tilde{Q}(t_1 + t_1^p)}{2}\right\}, \tag{23}$$

and

$$\langle I_y\rangle(t_1 + t_1^p) = 0. \tag{24}$$

Recalculating the above for $\phi \neq 0$, we obtain the following:

$$\tilde{\mathbf{H}}_1^* = -\frac{\hbar\omega_1}{\sqrt{2}}\begin{pmatrix} 0 & e^{-i\phi} & 0 \\ e^{i\phi} & 0 & e^{i\phi} \\ 0 & e^{-i\phi} & 0 \end{pmatrix}, \tag{25}$$

$$\tilde{\rho}(t_1^p) \propto \frac{\beta\hbar\tilde{Q}}{2}\left\{\begin{pmatrix} 1 & 0 & \eta \\ 0 & -2 & 0 \\ \eta & 0 & 1 \end{pmatrix} + \frac{(\eta+3)i}{2\sqrt{2}}\begin{pmatrix} 0 & -e^{-i\phi} & 0 \\ e^{i\phi} & 0 & e^{i\phi} \\ 0 & -e^{-i\phi} & 0 \end{pmatrix}\sin(2\omega_1 t_1^p) + \frac{(\eta+3)}{4}\begin{pmatrix} 1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & 1 \end{pmatrix}[\cos(2\omega_1 t_1^p) - 1]\right\}, \tag{26}$$

$$\langle I_x\rangle(t_1 + t_1^p) \propto \tfrac{1}{2}\beta\hbar\tilde{Q}(\eta + 3)\sin(2\omega_1 t_1^p)\sin\left\{\frac{(\eta + 3)\tilde{Q}(t_1 + t_1^p)}{2} - \phi\right\}, \tag{27}$$

and

$$\langle I_y\rangle(t_1 + t_1^p) = 0. \tag{28}$$

It must be noted that the factor $\omega_{1,\text{eff}}$ which appears in our previous treatment for integer spins ([2], equation (32)) is incorrect in the absence of an external magnetic field for transitions $|10\rangle \rightarrow |1 \pm 1\rangle$. In addition to neglecting the non-secular contributions of the RF Hamiltonian for spin 1, the contribution $[\mathbf{H}^+(t), \mathbf{H}^-(t)]$ due to the common level was also ignored in [2].

The results for a spin 3/2 system subject to a RF pulse with an arbitrary phase can be obtained in an analogous manner. The effective RF Hamiltonian in the quadrupole interaction frame is given by

$$\begin{aligned}\tilde{\mathbf{H}}_1(t) = -2\hbar\gamma H_1\cos(\omega t - \phi)\Bigg[I_x &+ \frac{i(\eta + 3)}{2(\eta^2 + 3)^{1/2}}\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \\ &\times \sin[\chi(12(\eta^2 + 3))^{1/2}] \\ &- \frac{\eta + 3}{2(\eta^2 + 3)}\begin{pmatrix} 0 & -\sqrt{3} & 0 & \eta \\ -\sqrt{3} & 0 & -\eta & 0 \\ 0 & -\eta & 0 & -\sqrt{3} \\ \eta & 0 & -\sqrt{3} & 0 \end{pmatrix} \\ &\times \{\cos[\chi(12(\eta^2 + 3))^{1/2}] - 1\}\Bigg]\end{aligned} \tag{29}$$

where $\chi = \tilde{Q}t/6$. The secular part of this Hamiltonian is identified to be

$$\tilde{\mathbf{H}}_1^* = -\hbar\omega_1\begin{pmatrix} 0 & a_1 & 0 & a_2 \\ a_1^* & 0 & -a_2 & 0 \\ 0 & -a_2 & 0 & a_1^* \\ a_2 & 0 & a_1 & 0 \end{pmatrix}, \tag{30}$$

where

$$a_1 = \frac{\eta + 3}{2(\eta^2 + 3)}[\sqrt{3}\cos\phi + i(\eta^2 + 3)^{1/2}\sin\phi],$$

$$a_1^* = \frac{\eta + 3}{2(\eta^2 + 3)}[\sqrt{3}\cos\phi - i(\eta^2 + 3)^{1/2}\sin\phi]$$

and

$$a_2 = \frac{\eta + 3}{2(\eta^2 + 3)}[-\eta\cos\phi].$$

It should be noted that the simplicity of the $I = 1$ case in which the secular Hamiltonian is independent of η is lost in this case on account of the complicated η dependence of $\tilde{\mathbf{H}}_1^*$ (and for higher values such as $I = 2, 5/2$ etc.). However, the BCH theorem can still be applied successfully to the above to give

$$\tilde{\rho}(t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{6}\left\{\begin{pmatrix} -3 & 0 & -\eta\sqrt{3} & 0 \\ 0 & 3 & 0 & -\eta\sqrt{3} \\ -\eta\sqrt{3} & 0 & 3 & 0 \\ 0 & -\eta\sqrt{3} & 0 & -3 \end{pmatrix}\cos\left[\frac{\omega_1 t_1^\rho(\eta+3)}{(\eta^2+3)^{1/2}}\right] + i\frac{(\eta^2+3)^{1/2}}{(\eta+3)}\sin\left[\frac{\omega_1 t_1^\rho(\eta+3)}{(\eta^2+3)^{1/2}}\right]\begin{pmatrix} 0 & a_3 & 0 & a_4 \\ -a_3^* & 0 & -a_4 & 0 \\ 0 & -a_4 & 0 & -a_3^* \\ a_4 & 0 & a_3 & 0 \end{pmatrix}\right\}, \quad (31)$$

where

$$a_3 = \frac{\eta+3}{(\eta^2+3)^{1/2}}[\sqrt{3}\cos\phi + 3i\sin\phi],$$

$$-a_3^* = \frac{\eta+3}{(\eta^2+3)^{1/2}}[-\sqrt{3}\cos\phi + 3i\sin\phi]$$

and

$$a_4 = \frac{\eta+3}{(\eta^2+3)^{1/2}}[-i\eta\sqrt{3}\sin\phi].$$

This leads to the following expressions for expectation values of $\langle I_x\rangle$ and $\langle I_y\rangle$, namely

$$\langle I_x\rangle(t_1 + t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}(\eta+3)}{\sqrt{3}}\sin\left\{\frac{\omega_1 t_1^\rho(\eta+3)}{(\eta^2+3)^{1/2}}\right\}\sin\left((12(\eta^2+3))^{1/2}\chi - \phi\right) \quad (32)$$

where $\chi = \frac{\tilde{Q}(t_1 + t_1^\rho)}{6}$, and

$$\langle I_y\rangle(t_1 + t_1^\rho) = 0. \quad (33)$$

4. Validity of ignoring non-secular terms

In this section, we study the validity of ignoring non-secular components of the effective RF Hamiltonians for spin 1, as done in going from equation (16) to equation (17). In particular, we calculate $\langle I_x(t)\rangle$ from equation (14) with $\phi = 0$, which involves both $\tilde{I}_x(t)$ and $\tilde{\rho}(t)$. The evaluation of $\tilde{I}_x(t)$ is unchanged from that given earlier, leading to the form given in the square brackets of equation (16). The expression given for $\tilde{\rho}$ in section 3, however, is not valid, since its solution from equation (12) for a time-dependent Hamiltonian is not given by equation (13) but by a Dyson time-ordered expansion or Magnus expansion [1]. For the present purpose, however, we restrict ourselves to the lowest order in a Magnus expansion scheme and calculated $\tilde{\rho}(t)$ by

$$\tilde{\rho}(t) \approx \exp\left\{-\frac{i}{\hbar}\int_0^t ds\tilde{\mathbf{H}}_1(s)\right\}\rho(0)\exp\left\{\frac{i}{\hbar}\int_0^t ds\,\tilde{\mathbf{H}}_1(s)\right\}. \tag{34}$$

Substituting $\tilde{\mathbf{H}}_1(t)$, and setting the quadrupole frequency to $\omega_Q = (\eta + 3)\tilde{Q}/2$ leads to

$$\frac{i}{\hbar}\int_0^t ds\,\tilde{\mathbf{H}}_1(s) = \begin{pmatrix} 0 & f & 0 \\ g & 0 & g \\ 0 & f & 0 \end{pmatrix}, \tag{35}$$

where integration over the trigonometric function gives

$$f = \frac{\omega_1}{(\omega^2 - \omega_Q^2)\sqrt{2}}\left[(\omega - \omega_Q)\exp(i(\omega + \omega_Q)t) - (\omega + \omega_Q)\exp(-i(\omega - \omega_Q)t) + 2\omega_Q\right] \tag{36}$$

and

$$g = \frac{\omega_1}{(\omega^2 - \omega_Q^2)\sqrt{2}}\left[-(\omega - \omega_Q)\exp(-i(\omega + \omega_Q)t) + (\omega + \omega_Q)\exp(i(\omega - \omega_Q)t) - 2\omega_Q\right]. \tag{37}$$

Note that

$$g = -f^*,$$

and that the product is given by

$$fg = \frac{\omega_1^2}{(\omega^2 - \omega_Q^2)^2}\{-(\omega^2 + 3\omega_Q^2) + (\omega^2 - \omega_Q^2)\cos(2\omega t) - 2\omega_Q(\omega - \omega_Q)\cos[(\omega + \omega_Q)t] + 2\omega_Q(\omega + \omega_Q)\cos[(\omega - \omega_Q)t]\}. \tag{38}$$

Substitution of expression (35) into (34) and subsequent use of MAPLE results in the following expression for the density matrix,

$$\tilde{\rho}(t) \propto \frac{\beta\hbar\tilde{Q}}{2}\left\{ I_Q(\eta) - i(\eta + 3)\frac{\sin(-i(8fg)^{1/2})}{(8fg)^{1/2}}\begin{pmatrix} 0 & -f & 0 \\ g & 0 & g \\ 0 & -f & 0 \end{pmatrix} - \frac{\eta + 3}{4}[\cos(-i(8fg)^{1/2}) - 1]\begin{pmatrix} 1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & 1 \end{pmatrix}\right\}. \tag{39}$$

We obtain the expectation value of I_x from expression (39), which now contains both secular and non-secular contributions,

$$\langle I_x \rangle(t) \propto \frac{\beta\hbar\tilde{Q}}{2}(\eta + 3)\left[-\sqrt{2}(f + g)\frac{\sin(-i(8fg)^{1/2})}{(8fg)^{1/2}}\sin(\omega_Q t) - i\sqrt{2}(f - g)\frac{\sin(-i(8fg)^{1/2})}{(8fg)^{1/2}}\cos(\omega_Q t)\right]. \tag{40}$$

To proceed further, we investigate this equation in the limit $\omega_Q \gg \omega_1$ as the carrier frequency ω approaches ω_Q. From expressions (36)–(38) the limits are obtained as

$$\lim_{\omega \to \omega_Q} f = \frac{i\omega_1 t}{\sqrt{2}}$$

$$\lim_{\omega \to \omega_Q} g = \frac{i\omega_1 t}{\sqrt{2}}$$

$$\lim_{\omega \to \omega_Q} i(8fg)^{1/2} = -2\omega_1 t$$

$$\lim_{\omega \to \omega_Q} \left(\frac{f}{g}\right)^{1/2} = 1,$$

all of which are to order (ω_1/ω_Q). Since this frequency ratio (ω_1/ω_Q) must be small for the limits to be meaningful, the quadrupole frequency must dominate the RF amplitude. These limits are thus valid for weak pulses applied to quadrupolar systems. Substitution of these limits into expression (39) yields results in agreement with (19). We conclude that, under these conditions, the secular approximation used in section 3 is valid.

5. Rotating and counter-rotating contributions

In this section, the secular approach described in section 3 is used to calculate the effects of circularly polarized RF fields. To this end the RF Hamiltonian (6) with $\phi = 0$ is decomposed into

$$\mathbf{H}_1(t) = \mathbf{H}_1^+(t) + \mathbf{H}_1^-(t), \tag{41}$$

where

$$\mathbf{H}_1^{\pm}(t) = -\hbar\omega_1[I_x \cos \omega t \mp I_y \sin \omega t]$$

with the + sign being used to denote 'rotating' component and the − sign to denote the 'counter-rotating' component. Clearly, the relationship $\mathbf{H}_1^+(-\omega, t) = \mathbf{H}_1^-(\omega, t)$ holds, so the results of one are related easily to those of the other. The calculation follows from that of section 3, with $\tilde{\mathbf{H}}_1(t)$ being replaced by

$$\tilde{\mathbf{H}}_1^-(t) = -\hbar\omega_1\left\{\cos \omega t\left[\frac{i}{\sqrt{2}}\sin(\omega_Q^- t)\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + \frac{1}{\sqrt{2}}\cos(\omega_Q^- t)\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\right]\right.$$
$$\left. + \sin \omega t\left[\frac{1}{\sqrt{2}}\sin(\omega_Q^+ t)\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} + \frac{i}{\sqrt{2}}\cos(\omega_Q^+ t)\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}\right]\right\}, \tag{42}$$

where

$$\omega_Q^{\pm} = \frac{(\eta \pm 3)\tilde{Q}}{2}.$$

This result, in contrast to expression (16), demonstrates that there are two secular components, $\omega = \omega_Q^+$ and $\omega = \omega_Q^-$, both of which must be retained.

On collecting the trigonometric terms, equation (42) reduces to

$$\tilde{\mathbf{H}}_1^-(t) = -\frac{\hbar\omega_1}{\sqrt{2}}\begin{pmatrix} 0 & f & 0 \\ f^* & 0 & g^* \\ 0 & g & 0 \end{pmatrix}, \tag{43}$$

where now, after simplification, f and g are given by

$$f = \tfrac{1}{2}[\exp(i(\omega + \omega_Q^-)t) + \exp(-i(\omega - \omega_Q^-)t) - \exp(i(\omega + \omega_Q^+)t) + \exp(-i(\omega - \omega_Q^+)t)] \tag{44}$$

and

$$g = \tfrac{1}{2}[\exp(i(\omega - \omega_Q^-)t) + \exp(-i(\omega + \omega_Q^-)t) + \exp(i(\omega + \omega_Q^+)t) - \exp(-i(\omega - \omega_Q^+)t)] \tag{45}$$

Retaining the two secular contributions ($f = 1, g = 0$) gives the desired result,

$$\tilde{\mathbf{H}}_1^-{}^* = -\frac{\hbar\omega_1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{46}$$

The corresponding result for $\tilde{\mathbf{H}}_1^+{}^*$, the rotating component, can be obtained by substituting $-\omega$ for ω in equations (44) and (45) and is given (for $f = 0$ and $g = 1$) by

$$\tilde{\mathbf{H}}_1^+{}^* = -\frac{\hbar\omega_1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{47}$$

Clearly, $\tilde{\mathbf{H}}_1^+{}^*$ and $\tilde{\mathbf{H}}_1^-{}^*$ do not commute, i.e.,

$$[\tilde{\mathbf{H}}_1^+{}^*, \tilde{\mathbf{H}}_1^-{}^*] = \frac{\hbar^2\omega_1^2}{2}\begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

Moreover, summing the two oppositely rotating components gives $\tilde{\mathbf{H}}_1^*$ of section 3, so that $\tilde{\rho}(t)$ and $\langle I_x \rangle(t)$ obtained from the sum of rotating and counter-rotating components will have the correct limit (see the previous section for taking the appropriate limit).

In [2], spins 1 and 3/2 were treated with the use of rotating and counter-rotating components *separately* to calculate the effects on two transitions:

$$\mathbf{H}^+(t) \quad \text{for} \quad M \to M + 1$$

and

$$\mathbf{H}^-(t) \quad \text{for} \quad -M \to -(M + 1)$$

In terms of the present notation, the effects of a pulse may be described by retaining the secular contributions according to

$$\tilde{\rho}(t) = \exp\left\{-\frac{i\tilde{\mathbf{H}}_1^{+*}t}{\hbar}\right\}\exp\left\{-\frac{i\tilde{\mathbf{H}}_1^{-*}t}{\hbar}\right\}\tilde{\rho}(0)\exp\left\{\frac{i\tilde{\mathbf{H}}_1^{-*}t}{\hbar}\right\}\exp\left\{\frac{i\tilde{\mathbf{H}}_1^{+*}t}{\hbar}\right\} \tag{48}$$

and neglecting the non-commutation between the two components. The approach reproduces the results correctly based on the secular approximation independently of the spin magnitude for all but one case. This article shows that the secular approximation needs to be implemented for each spin magnitude separately, and that the algebra can get quite out of hand very quickly unless one uses a simple matrix representation for the spin density operator. It can be done virtually error-free with the use of a symbolic manipulation such as MAPLE. It does provide consistent results for all cases, though it lacks the physical intuition which goes with [2] where the selective nature of the NQR pulses was exploited. The one case for which the approach described in [2] leads to inconsistent results for pure NQR is the case in which the RF irradiation excites transition from a common level, namely the lowest level in integer spin systems (for $\eta = 0$, this is the $|I0\rangle$ level). This point underscores one fundamental difference in NMR and NQR. In NMR, it is sufficient to retain only one of the circularly polarizing components of the RF field for selective excitation. In the case of NQR, it is necessary to include both components, as was demonstrated in [2], or, equivalently, proceed with the secular approximation using the linearly polarized RF irradiation.

6. Results for $I = 2$

The analysis of the effect of RF pulses in integer spins with $I \geqslant 2$ is carried out most easily with the quadrupole Hamiltonian in a diagonal representation. The correspondence between quadrupole Hamiltonian for integer spins and the rigid asymmetric rotor Hamiltonian used in microwave spectroscopy [20, 21] enables us to obtain the eigenvalues and eigenvectors of the quadrupole Hamiltonian for $I = 2$ and $I = 3$ quite easily. We therefore employ the basis in which $I_Q(\eta)$ is diagonal in order to evaluate the effect of RF pulses on integer spins, using computer algebra to provide the details of the eigenvalue problem. The method is summarized here for $I = 2$, yet it can be extended to spins $I > 2$. It is shown that the results given here reduce to those of [2] in the limit of $\eta = 0$ if one replaces $\omega_{1,\text{eff}}$ by a corresponding factor only for the $0 \to \pm 1$ transitions. We emphasize that the example of $I = 2$ chosen here is only for the purposes of illustration of a more general scheme for integer I. We do note, however, that long-lived radioisotopes with nuclear spin $I = 2$ and significant electric quadrupole moment are known to exist and that stable nuclei with non-zero spin have either half-integer or odd integer values for I [22]. In order to simplify the algebra involved in the evaluation of $\tilde{I}_x$ for spins with $I = 2$ using expression (15), we introduce here the unitary transformation matrix which diagonalizes $I_Q(\eta)$ for $I = 2$. Denoting the matrix of eigenvalues of $I_Q(\eta)$ by I_Q^{dia} where

$$I_Q^{\text{dia}} = uI_Q(\eta)u^{\text{T}}, \tag{49}$$

$\tilde{I}_x$ can be rewritten as

$$\tilde{I}_x = u^{\text{T}} \exp(i\chi I_Q^{\text{dia}})uI_xu^T \exp(-i\chi I_Q^{\text{dia}})u. \tag{50}$$

For completeness, the specific eigenvalues of $I_Q(\eta)$ are

$$\lambda_1 = -6,$$

$$\lambda_2 = 3 - 3\eta,$$

$$\lambda_3 = 6(1 + \eta^2/3)^{1/2},$$

$$\lambda_4 = 3 + 3\eta,$$

$$\lambda_5 = -6(1 + \eta^2/3)^{1/2}.$$

Straightforward but lengthy algebra gives three secular forms from $\tilde{\mathbf{H}}_1$, which correspond to three different transitions being caused by I_x, and these are denoted as $\tilde{\mathbf{H}}_1^{25*}$, $\tilde{\mathbf{H}}_1^{23*}$ and $\tilde{\mathbf{H}}_1^{14*}$, respectively. For $\chi = \tilde{Q}t/12$, these secular parts of $\tilde{\mathbf{H}}_1^*$ at each RF transition-causing pulse are

$$\tilde{\mathbf{H}}_1^{25*} = -\hbar\omega_1 \begin{pmatrix} 0 & a & 0 & a & 0 \\ a & 0 & A & 0 & a \\ 0 & A & 0 & A & 0 \\ a & 0 & A & 0 & a \\ 0 & a & 0 & a & 0 \end{pmatrix}, \tag{51}$$

$$\tilde{\mathbf{H}}_1^{23*} = -\hbar\omega_1 \begin{pmatrix} 0 & b & 0 & b & 0 \\ b & 0 & B & 0 & b \\ 0 & B & 0 & B & 0 \\ b & 0 & B & 0 & b \\ 0 & b & 0 & b & 0 \end{pmatrix}, \tag{52}$$

and

$$\tilde{\mathbf{H}}_1^{14*} = -\frac{\hbar\omega_1}{2} \begin{pmatrix} 0 & 1 & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 & 0 \end{pmatrix}. \tag{53}$$

The parameters characterizing the secular Hamiltonians are

$$a = \frac{\eta^2 + 3 + (1 + \eta)(9 + 3\eta^2)^{1/2}}{4(\eta^2 + 3)},$$

$$b = \frac{\eta^2 + 3 - (1 + \eta)(9 + 3\eta^2)^{1/2}}{4(\eta^2 + 3)},$$

$$A = \frac{3\eta^2 + 9 + (\eta - 3)(9 + 3\eta^2)^{1/2}}{2\sqrt{6}(\eta^2 + 3)}$$

and

$$B = \frac{3\eta^2 + 9 - (\eta - 3)(9 + 3\eta^2)^{1/2}}{2\sqrt{6}(\eta^2 + 3)}.$$

These secular Hamiltonians are given in a superscripted form corresponding to the RF frequencies $\omega_{25} = \tilde{Q}(\lambda_2 - \lambda_5)/12$, $\omega_{23} = \tilde{Q}(\lambda_2 - \lambda_3)/12$ and $\omega_{14} = \tilde{Q}(\lambda_1 - \lambda_4)/12$, respectively. The simplicity of $\tilde{\mathbf{H}}_1^{14*}$ allows the BCH formalism to be employed successfully for its determination of the associated $\tilde{\rho}(t_1^\rho)$. Applying the eigenvector method described for $\tilde{\mathbf{H}}_1^*$ with $\omega = \omega_{14}$ gives the corresponding density matrix (for $\phi = 0$)

$$\tilde{\rho}_{14}(t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{12}\left[I_Q(\eta) + \frac{3i}{4}(\eta + 3)\sin(2\omega_1 t_1^\rho)\begin{pmatrix} 0 & 1 & 0 & -1 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 1 & 0 \end{pmatrix} \right.$$
$$\left. - \tfrac{3}{4}(\eta + 3)[\cos(2\omega_1 t_1^\rho) - 1]\begin{pmatrix} 1 & 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ -1 & 0 & 0 & 0 & 1 \end{pmatrix}\right]. \quad (54)$$

Combining this with $\tilde{I}_x(t_1 + t_1^\rho)$ gives the average I_x expectation value as

$$\langle I_x \rangle (t_1 + t_1^\rho) \propto -\frac{\beta\hbar\tilde{Q}(\eta + 3)}{4\sqrt{10}} \sin(2\omega_1 t_1^\rho) \sin\left\{\frac{(\eta + 3)}{4}\tilde{Q}(t_1 + t_1^\rho)\right\}. \quad (55)$$

Similar, albeit more complicated, forms can be found for $\tilde{\rho}_{25}(t_1^\rho)$ and $\tilde{\rho}_{23}(t_1^\rho)$, the density matrices corresponding to the $\omega = \omega_{25}$ and $\omega = \omega_{23}$ RF transitions. Omitting these details, the spin averages along I_x resulting from $\omega = \omega_{25}$ are

$$\langle I_x \rangle (t_1 + t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{12\sqrt{5}} \frac{-\eta + 3 - (9 + 3\eta^2)^{1/2}}{(\eta^2 + 3 - (9 + 3\eta^2)^{1/2})^{3/2}}$$
$$\times [-3(\eta + 1)(\eta^2 + 3) + (2\eta^2 + 3\eta + 3)(9 + 3\eta^2)^{1/2}]$$
$$\times \sin\left\{2\omega_1 t_1^\rho \left(2 - \frac{(1 - \eta)(9 + 3\eta^2)^{1/2}}{\eta^2 + 3}\right)\right\} \sin\left\{(\lambda_2 - \lambda_5)\frac{\tilde{Q}(t_1 + t_1^\rho)}{12}\right\}. \quad (56)$$

For $\omega = \omega_{23}$, the average $\langle I_x \rangle$ is

$$\langle I_x \rangle (t_1 + t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{12\sqrt{5}} \frac{-\eta + 3 + (9 + 3\eta^2)^{1/2}}{(\eta^2 + 3 + (9 + 3\eta^2)^{1/2})^{3/2}}$$
$$\times [-3(\eta + 1)(\eta^2 + 3) - (2\eta^2 + 3\eta + 3)(9 + 3\eta^2)^{1/2}]$$
$$\times \sin\left\{2\omega_1 t_1^\rho \left(2 + \frac{(1 - \eta)(9 + 3\eta^2)^{1/2}}{\eta^2 + 3}\right)\right\} \sin\left\{(\lambda_2 - \lambda_3)\frac{\tilde{Q}(t_1 + t_1^\rho)}{12}\right\}. \quad (57)$$

7. Results for $I = 5/2$: the axially symmetric case

From $\mathbf{H}_Q = -\hbar\tilde{Q}I_Q(\eta)/10$ in the earlier notation, it can be shown that the BCH expansion gives $\tilde{I}_x$ (in slightly different format) as

$$\tilde{I}_x(t_1^\rho) = \begin{pmatrix} 0 & \sqrt{\tfrac{5}{2}}e^{-12\chi i} & 0 & 0 & 0 & 0 \\ \sqrt{\tfrac{5}{2}}e^{12\chi i} & 0 & \sqrt{2}e^{-6\chi i} & 0 & 0 & 0 \\ 0 & \sqrt{2}e^{6\chi i} & 0 & \tfrac{3}{2} & 0 & 0 \\ 0 & 0 & \tfrac{3}{2} & 0 & \sqrt{2}e^{6\chi i} & 0 \\ 0 & 0 & 0 & \sqrt{2}e^{-6\chi i} & 0 & \sqrt{\tfrac{5}{2}}e^{12\chi i} \\ 0 & 0 & 0 & 0 & \sqrt{\tfrac{5}{2}}e^{-12\chi i} & 0 \end{pmatrix}, \tag{58}$$

where $\chi = \tilde{Q}t_1^\rho/10$. By direct application of the BCH theorem, it can be shown that there are two contributions to $\tilde{\rho}(t)$ which arise from the 6χ and 12χ parts, here aptly denoted by $\tilde{\rho}_6(t)$ and $\tilde{\rho}_{12}(t)$, respectively, where

$$\tilde{\rho}_6(t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{10}\left[I_Q(0) + 3i\sin(2\sqrt{2}\omega_1 t_1^\rho) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \right.$$
$$\left. + 3[\cos(2\sqrt{2}\omega_1 t_1^\rho) - 1] \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \right] \tag{59}$$

and

$$\tilde{\rho}_{12}(t_1^\rho) \propto \frac{\beta\hbar\tilde{Q}}{10}\left[I_Q(0) + 6i\sin(\sqrt{5}\omega_1 t_1^\rho) \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \right.$$
$$\left. + 6[\cos(\sqrt{5}\omega_1 t_1^\rho) - 1] \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \right] \tag{60}$$

These contrasting forms of $\tilde{\rho}_6(t_1^\rho)$ and $\tilde{\rho}_{12}(t_1^\rho)$ may be combined with the expression for $\tilde{I}_x(t_1 + t_1^\rho)$, $[\chi = \tilde{Q}(t_1 + t_1^\rho)/10$ in equation (58)], to allow evaluation of their respective contributions to the $\langle I_x \rangle$ at the different RF frequencies. It can be seen that previous steps in calculating $\langle I_x \rangle$ give

$$\langle I_x \rangle_6(t_1 + t_1^\rho) \propto \frac{6\sqrt{2}}{5} \beta\hbar\tilde{Q} \sin(2\sqrt{2}\omega_1 t_1^\rho) \sin\left\{\frac{3\tilde{Q}(t_1 + t_1^\rho)}{5}\right\} \tag{61}$$

and

$$\langle I_x \rangle_{12}(t_1 + t_1^\rho) \propto \frac{6\sqrt{5}}{5} \beta\hbar\tilde{Q} \sin(\sqrt{5}\omega_1 t_1^\rho) \sin\left\{\frac{6\tilde{Q}(t_1 + t_1^\rho)}{5}\right\} \tag{62}$$

respectively.

8. Conclusion

For some spins with asymmetric electric field gradient distribution ($\eta \neq 0$), the elucidation of the ensemble spin average $\langle I_x \rangle$ for non-interacting nuclear spins can be carried out giving closed form expressions for the density matrix $\tilde{\rho}(t)$ in the interaction picture. The astute use of the algebraic processing language MAPLE allows this to be done efficiently for the NQR case with the BCH expansion being invoked in most cases. It should be noted that each MAPLE subroutine was checked a number of times, especially for the $I = 2$ eigenvalue approach, where the threefold degeneracy of the $\lambda = 0$ eigenvalue does present certain difficulties in the determination of u. Nevertheless, this approach allows the elementary solution of the von Neumann equation to be obtained for non-zero η problems associated with spins $I = 1$, $3/2$ and 2, and for $\eta = 0$ for spin $I = 5/2$. In addition, the justification of the traditional omission of non-secular terms in $\tilde{\mathbf{H}}_1$ and the influence on $\tilde{\rho}$ has been partially examined and confirmed for this NQR study for $I = 1$ in detail.

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Appendix A

Baker–Campbell–Hausdorff theorem and its applications

There are two applications of the BCH theorem which are critical in this paper: first, the algebraic form of $\tilde{I}_x = \exp(i\chi I_Q) I_x \exp(-i\chi I_Q)$, from which $\tilde{\mathbf{H}}_1 = -2\hbar\omega_1 \cos(\omega t - \phi)\tilde{I}_x$ is found, and second the solution of the von Neumann equation as propagated by the secular part $\tilde{\mathbf{H}}_1^*$ of $\mathbf{H}_1$ (equation (13)). Both involve quantities of the form $\exp(A)B\exp(-A)$, which is given by the BCH expansion as

$$\exp(A)B\exp(-A) = B + [A, B] + \tfrac{1}{2}[A, [A, B]] + \frac{1}{3!}[A, [A, [A, B]]] + \cdots. \tag{A 1}$$

The recurring nature of this infinite series allows its sum to be evaluated directly using simple MAPLE code.

For $I = 1$,

$$B \equiv I_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad A \equiv i\chi I_Q(\eta) = -i\chi\begin{pmatrix} 1 & 0 & \eta \\ 0 & -2 & 0 \\ \eta & 0 & 1 \end{pmatrix}, \tag{A 2}$$

and

$$\begin{aligned}\tilde{I}_x = &-\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}\left[(\eta+3)\frac{i\chi}{1!} + (\eta+3)^3\frac{(i\chi)^3}{3!} + (\eta+3)^5\frac{(i\chi)^5}{5!} + \cdots\right] \\ &+\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\left[1 + (\eta+3)^2\frac{(i\chi)^2}{2!} + (\eta+3)^4\frac{(i\chi)^4}{4!} + (\eta+3)^6\frac{(i\chi)^6}{6!} + \cdots\right] \\ = &-\frac{i}{\sqrt{2}}\sin[(3+\eta)\chi]\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + \frac{1}{\sqrt{2}}\cos[(3+\eta)\chi]\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.\end{aligned} \tag{A 3}$$

The only assumption involves retention of the condition $|(\eta + 3)\chi| < 1$ for the convergence of the trigonometric series.

Appendix B

The following MAPLE code gives the preliminary steps in the derivation of $\tilde{\rho}(t_1^\rho)$ in expression (19) from the secular Hamiltonian defined in equation (17). For convenience, the factor of $-\hbar\omega_1/\sqrt{2}$ has been omitted.

```
# this maple program calcs rho~(t) for spin =1
i:=1;
nsize:=2*i+1;
alias( Id = &*());
i_plus:=array(sparse,1..nsize,1..nsize): i_minus:=array(1..nsize,1..nsize):
i_x:=array(1..nsize,1..nsize):
i_y:=array(1..nsize,1..nsize): i_z:=array(sparse,1..nsize,1..nsize):
i_q:=array(sparse,1..nsize,1..nsize):
eih1t:=array(sparse,1..nsize,1..nsize): i_eta:=array(1..nsize,1..nsize);

#

#get the i_plus, i_z and i_q matrices.
i_row:=1;
for m from -i to i-1 do
```

```
i_plus[i_row,i_row+1]:=sqrt((i+m+1)*(i-m));
i_q[i_row,i_row]:=i*(i+1)-3*m**2;
i_z[i_row,i_row]:= -m;
i_row:= i_row + 1;
od;
i_z[i_row,i_row]:= -i;
i_q[i_row,i_row]:=i*(i+1)-3*i**2;
#
i_minus:=evalm(transpose(i_plus));
#
# eih1t is (-i* h(tilde)1*t/hbar) operator
#
i_x:=evalm(i_plus + i_minus)/2;
i_y:=evalm((i_plus - i_minus)/(2*I));
#
# for spin = 1
# for phi = 0 for I_x pulse use the next 3 lines of code
#
i_eta:=array(1..nsize,1..nsize,[[0,1,0],
[1,0,1],
[0,1,0]]);
i_qeta:=evalm(i_q - eta/2*(i_plus&*i_plus+i_minus&*i_minus));
eih1t:=evalm(i_eta);
p0:=evalm(i_qeta);
for j from 1 to 3* (2*i+1) do
p.j:=evalm(eih1t&*p.(j-1) - p.(j-1)&*eih1t):
map(evalc,p.j):
od;
evalm(i_qeta);
for j from 1 to 3* (2*i+1) do
map(simplify,evalm(p.j/(3+eta)))*(3+eta);
od;
#
```

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