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# Some analytical results for *ABC*, *ABCD*, and *XBCD* coupled spin 1/2 systems. II

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In the preceding paper, it was shown that the calculation of the density matrix $\rho(t)$ for multiply connected *ABC*, etc., spin 1/2 spin systems can be greatly simplified by subdividing the Hamiltonian $\mathcal{H}$ into $(\mathcal{H}_1 + \mathcal{H}_2)$, where $\mathcal{H}_1$ is a suitable linear combination of the constants of the motion. In this paper, a framework for the determination of the time evolution of high-order multipolar quantum states is presented and discussed. It is shown that the necessary mathematical labour is reduced to a minimum by (i) exploiting the fact that $\mathcal{J}_z$ is a good quantum number, and (ii) using the theory of partitioned matrices. For example, it is shown that for a general $n$-coupled spin 1/2 system, the spin dynamics of the $Q = \pm K_{\max}$ $(\pm K_{\max} \mp 1)$ multipolar states, where $K_{\max}$ is the maximum tensorial rank, can be determined without the need to diagonalize the full $2^n \times 2^n$ Hamiltonian matrix, where $n$ is the number of spins. In fact, to describe the time evolution of the $Q = (\pm K_{\max} \mp 1)$ multipolar states it is only necessary to diagonalize two $n \times n$ matrices at most. Finally, some cautionary remarks are made concerning the use of the "weak-coupling approximation".

## 1. Introduction

In the preceding paper [1], it was shown that the determination of the time dependent density matrix $\rho(t)$, for *ABC*, etc., coupled spin 1/2 spin systems, can be greatly simplified by subdividing the Hamiltonian

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 , \tag{1}$$

where $\mathcal{H}_1$ commutes with $\mathcal{H}$. In practice, this is achieved by first identifying the constants of the motion for $\mathcal{H}$, and then choosing $\mathcal{H}_1$ to be a suitable combination of the constants of the motion. Further, it was also demonstrated that if $K_{\max}$ is the maximum rank available to the spin system, tensor operators of the form $\hat{\mathbf{T}}^{K_{\max}}_{\pm K_{\max}}(\mathbf{k})$ are simple constants of the motion under the action of $\mathcal{H}_2$. Such operators only evolve in a Zeeman-like fashion under the action of $\mathcal{H}_1$.

In this paper, the problem of determining the evolution of high-order tensor operators $\hat{\mathbf{T}}^{K}_{\pm Q}(\mathbf{k})$ is addressed, where the order $Q$ is less than the maximum rank tensor $K_{\max}$ available to the spin system. For example, we shall be specifically concerned with the time evolution of the multiple quantum states $Q = \pm 2$ for the *ABC*

spin 1/2 coupled systems, and $Q = \pm 3$ for $ABCD$ spin systems. It is, of course, well known that the number of lines in a multiple quantum (MQ) NMR experiment is reduced as the MQ order is increased [2]. This is due to the reduction in the number of "allowed" transitions as $\Delta m$ is increased. However, in this paper it will be shown that the determination of the time evolution of high order tensors does not require a full diagonalization of the $2^n \times 2^n$ matrix for a $n$-coupled spin 1/2 spin system. In fact, to determine the time evolution of the $Q = \pm K_{\max} \mp 1$ multipolar states, it is only necessary to diagonalize at most two $n \times n$ matrices.

Finally, all the definitions and notations used in this paper follow those of the preceding paper.

## 2. A three spin 1/2 scalar coupled $ABC$ spin system

For the $ABC$ spin 1/2 spin system discussed in [1], it can be shown that $\mathcal{H}_1$ and $\mathcal{H}_2$ can be expressed in the partitioned form

$$\mathcal{H}_1/\hbar = \begin{array}{c|cccc} & 0 & 1 & 1' & 0' \\ 0 & a_1 & 0 & 0 & 0 \\ 1 & 0 & \mathbf{b}_1 & 0 & 0 \\ 1' & 0 & 0 & \mathbf{c}_1 & 0 \\ 0' & 0 & 0 & 0 & d_1 \end{array}, \qquad \mathcal{H}_2/\hbar = \begin{array}{c|cccc} & 0 & 1 & 1' & 0' \\ 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \mathbf{b}_2 & 0 & 0 \\ 1' & 0 & 0 & \mathbf{c}_2 & 0 \\ 0' & 0 & 0 & 0 & 0 \end{array} \tag{2}$$

where the $1 \times 1$ $a_1$ and $d_1$ matrices, and $3 \times 3$ $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{c}_1$, $\mathbf{c}_2$ matrices are summarized in Table 1. Here the $8 \times 8$ Hamiltonian matrix has been partitioned using the ficti-

Table 1
The matrices, $a_1$, $\mathbf{b}_1$, $\mathbf{c}_1$, $d_1$, and $a_2$, $\mathbf{b}_2$, $\mathbf{c}_2$, $d_2$ for the Hamiltonian of eq. (2).

$a_1 = \frac{3}{2}\Delta\bar{\omega} + \frac{3}{4}\bar{J}$ $(\mathcal{J}_z = +3/2)$; $d_1 = \frac{3}{2}\Delta\bar{\omega} + \frac{3}{4}\bar{J}$ $(\mathcal{J}_z = -3/2)$

$$\mathbf{b}_1 = \begin{bmatrix} \frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} & 0 & 0 \\ 0 & \frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} & 0 \\ 0 & 0 & \frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} \end{bmatrix}; \quad \mathbf{c}_1 = \begin{bmatrix} -\frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} & 0 & 0 \\ 0 & -\frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} & 0 \\ 0 & 0 & -\frac{1}{2}\Delta\bar{\omega} - \frac{1}{4}\bar{J} \end{bmatrix}$$

$(\mathcal{J}_z = +1/2)$ $(\mathcal{J}_z = -1/2)$

$a_2 = 0$ $(\mathcal{J}_z = +3/2)$; $d_2 = 0$ $(\mathcal{J}_z = -3/2)$

$$\mathbf{b}_2 = \begin{bmatrix} a + \Delta\omega_1 & J'_{BC} & J'_{AC} \\ J'_{BC} & b + \Delta\omega_2 & J'_{AB} \\ J'_{AC} & J'_{AB} & c + \Delta\omega_3 \end{bmatrix}; \quad \mathbf{c}_2 = \begin{bmatrix} a - \Delta\omega_1 & J'_{BC} & J'_{AC} \\ J'_{BC} & b - \Delta\omega_2 & J'_{AB} \\ J'_{AC} & J'_{AB} & c - \Delta\omega_3 \end{bmatrix}$$

$(\mathcal{J}_z = +1/2)$ $(\mathcal{J}_z = -1/2)$

tious spin labels $\{0, 1, 1', 0'\}$, as discussed by [4]. In this notation the spin label 0 corresponds to the single entry under $\mathcal{J}_z = 3/2$, 1 to the three entries under $\mathcal{J}_z = +1/2$, $1'$ to the three entries under $\mathcal{J}_z = -1/2$, and $0'$ to the single entry $\mathcal{J}_z = -3/2$. The fictitious spins 0 and $0'$, 1 and $1'$ simply refer to different parts of the original $8 \times 8$ matrix, and have no physical significance. They are used solely to simplify the necessary book-keeping, under various matrix manipulations. Note that the two $3 \times 3$ matrices $\mathbf{b}_2$ and $\mathbf{c}_2$ contain off-diagonal terms. In the weak coupling limit [3], these off-diagonal terms in $\mathcal{H}_2$ are often dropped, an approximation which holds well for non-degenerate spins in the high-field limit. In general however, such off-diagonal terms can cause considerable admixing between those states with the same $\mathcal{J}_z$ value. Finally, readers who are unfamiliar with non-square matrices should note that although the region spanned by $\langle 1|0\rangle$ appears to be square in eq. (2), it is in fact a $3 \times 1$ (null) rectangular matrix.

We are now in a position to make an easy observation. Since the first and last rows and the first and last columns in the $8 \times 8$ matrix of $\mathcal{H}_2$ and zero, the highest order tensor operators $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$ and $\mathbf{A}_-\mathbf{B}_-\mathbf{C}_-$ are constants of the motion under $\mathcal{H}_2$. Thus the evolution of the $Q = 3$ tensors is determined solely by $\mathcal{H}_1$, i.e.

$$e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+e^{+i\mathcal{H}_1 t/\hbar} = \mathbf{A}_+\mathbf{B}_+\mathbf{C}_+e^{-i3\Delta\bar{\omega}t}. \tag{3}$$

However, the evolution of the tensor operators $\mathbf{A}_+\mathbf{B}_+$, $\mathbf{A}_+\mathbf{C}_+$, $\mathbf{B}_+\mathbf{C}_+$, etc., summarized in Table 2, is a little more difficult to determine. These operators are close to but not exactly members of a basis set with well defined rotational properties. A more appropriate set can be seen in Table 3. Nevertheless, since both sets of operators occupy those parts of the matrix spanned by $\langle 0|1'\rangle$ and $\langle 1|0'\rangle$, the conclusions reached below are independent of which set is used.

Using the matrices set out in Table 2, the double quantum operators $\mathbf{A}_+\mathbf{B}_+$ can be written in the abbreviated form:

Table 2
The double quantum operators $\mathbf{A}_+\mathbf{B}_+$, etc. The numbers outside the matrices refer to the original labels of the *ABC* spin-labelling sequence [1].

$$\langle 0|\mathbf{B}_+\mathbf{C}_+|1'\rangle = \begin{array}{c} \\ 1 \end{array}\begin{array}{c} \begin{array}{ccc} 7 & 6 & 4 \end{array} \\ \boxed{\begin{array}{ccc} 0 & 0 & 1 \end{array}} \end{array} = \alpha$$

$$\langle 0|\mathbf{A}_+\mathbf{C}_+|1'\rangle = 1\ \boxed{\begin{array}{ccc} 0 & 1 & 0 \end{array}} = \beta$$

$$\langle 0|\mathbf{A}_+\mathbf{B}_+|1'\rangle = 1\ \boxed{\begin{array}{ccc} 1 & 0 & 0 \end{array}} = \gamma$$

$$\langle 1|\mathbf{B}_+\mathbf{C}_+|0'\rangle = \begin{array}{c} \\ 2 \\ 3 \\ 5 \end{array}\begin{array}{c} 8 \\ \boxed{\begin{array}{c} 0 \\ 0 \\ 1 \end{array}} \end{array} = \alpha'$$

$$\langle 1|\mathbf{A}_+\mathbf{C}_+|0'\rangle = \begin{array}{c} 2 \\ 3 \\ 5 \end{array}\boxed{\begin{array}{c} 0 \\ 1 \\ 0 \end{array}} = \beta'$$

$$\langle 1|\mathbf{A}_+\mathbf{B}_+|0'\rangle = \begin{array}{c} 2 \\ 3 \\ 5 \end{array}\boxed{\begin{array}{c} 1 \\ 0 \\ 0 \end{array}} = \gamma'$$

$$\mathbf{A}_+\mathbf{B}_+ = \begin{array}{c|cccc} & 0 & 1 & 1' & 0' \\ \hline 0 & 0 & 0 & \gamma & 0 \\ 1 & 0 & 0 & 0 & \gamma' \\ 1' & 0 & 0 & 0 & 0 \\ 0' & 0 & 0 & 0 & 0 \end{array} \tag{4}$$

Further, on invoking the nested commutator relationship,

$$\begin{aligned} \rho(t) &= e^{-i\mathcal{H}_1 t/\hbar}\rho(0)e^{+i\mathcal{H}_1 t/\hbar} \\ &= \rho(0) - \frac{it}{\hbar}[\mathcal{H}_1, \rho(0)] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2 [\mathcal{H}_1, [\mathcal{H}_1, \rho(0)]] - \ldots \end{aligned} \tag{5}$$

and substituting (2) and (4) into (5), we find after some minor manipulation

$$\begin{aligned} e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+\mathbf{B}_+e^{+i\mathcal{H}_1 t/\hbar} &= \gamma e^{-it(a_1-\mathbf{c}_1)} + e^{-it(\mathbf{b}_1-d_1)}\gamma' \\ &= \gamma e^{-ia_1 t}e^{+i\mathbf{c}_1 t} + e^{+id_1 t}e^{-i\mathbf{b}_1 t}\gamma', \end{aligned} \tag{6}$$

where we have made use of the fact that the $1 \times 1$ matrix $a_1$ commutes with the $3 \times 3$ matrix $\mathbf{c}_1$, etc. At first sight, the reader may have some difficulty in reconciling the idea that the exponential arguments can contain matrices of differing sizes. However, it should be born in mind that the both $\gamma$ and $\gamma'$ are $1 \times 3$ and $3 \times 1$ matrices, respectively. So when the exponentials are expanded, and multiplied by $\gamma$ and $\gamma'$, only $1 \times 3$ and $3 \times 1$ matrices remain, residing in those parts of the Hamiltonian matrix spanned by $\langle 0|1'\rangle$ and $\langle 1|0'\rangle$, respectively.

Eq. (6) can be simplified considerably. First, we observe that for $\mathcal{H}_1$, the $3 \times 3$ matrix $\mathbf{b}_1$ is diagonal with the triply degenerate eigenvalue $(1/2)(\Delta\bar{\omega} - \bar{J}/2)$. Similarly, matrix $\mathbf{c}_1$ is also triply degenerate with the eigenvalue $(1/2)(-\Delta\bar{\omega} - \bar{J}/2)$. Consequently, we can re-express (6) in the form

$$\begin{aligned} \rho_1(t) &= e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+\mathbf{B}_+e^{+i\mathcal{H}_1 t/\hbar} \\ &= \gamma e^{-i(\frac{3}{2}\Delta\bar{\omega}+\frac{3}{4}\bar{J})t}e^{+i(-\frac{1}{2}\Delta\bar{\omega}-\frac{1}{4}\bar{J})t} + \gamma' e^{+i(-\frac{3}{2}\Delta\bar{\omega}+\frac{3}{4}\bar{J})t}e^{-i(\frac{1}{2}\Delta\bar{\omega}-\frac{1}{4}\bar{J})t} \\ &= \gamma e^{-i(2\Delta\bar{\omega}+\bar{J})t} + \gamma' e^{-i(2\Delta\bar{\omega}-\bar{J})t}, \end{aligned} \tag{7}$$

a not entirely unexpected result. In essence, eq. (7) shows that the double quantum operators $\mathbf{A}_+\mathbf{B}_+$ ($\gamma$ and $\gamma'$) oscillates at the double quantum frequencies of $(2\Delta\bar{\omega} \pm \bar{J})$, respectively, under the action of $\mathcal{H}_1$. This is illustrated schematically in the left hand side of Fig. 1.

To complete our discussion of the evolution of the double quantum operator $\mathbf{A}_+\mathbf{B}_+$ it is now necessary to examine the evolution of the density $\rho_1(t)$ of (7) under $\mathcal{H}_2$. From an examination of (2), it will be observed that the problem is somewhat easier than that of $\mathcal{H}_1$ in that both $a_2$ and $d_2$ are identically equal to zero. However, the $3 \times 3$ matrices $\mathbf{b}_2$ and $\mathbf{c}_2$ are non-diagonal. Proceeding as before, we find

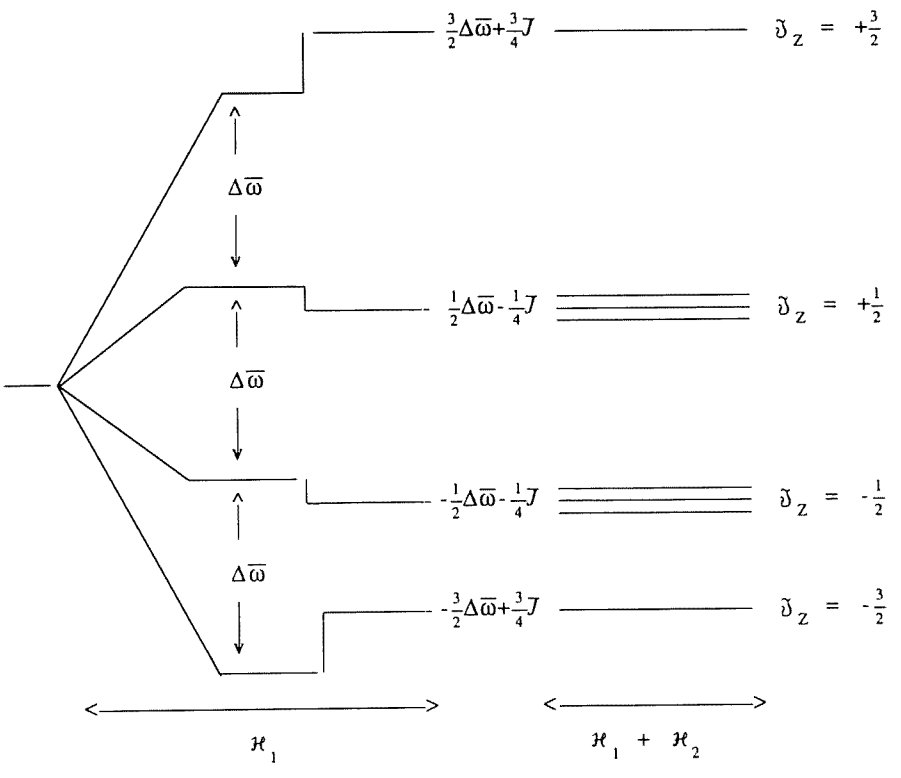


Fig. 1. The energy splitting of the $ABC$ spin system under the action of $\mathcal{H}_1$ and $\mathcal{H}_1 + \mathcal{H}_2$. The energy levels are labelled with the good quantum numbers $\mathcal{J}_z$. In all there are one triple quantum, six double quantum, and a maximum of fifteen single quantum frequencies.

$$\rho(t) = e^{-i\mathcal{H}t/\hbar}\mathbf{A}_+\mathbf{B}_+e^{+i\mathcal{H}t/\hbar} = e^{-i\mathcal{H}_2t/\hbar}\rho_1(t)e^{+i\mathcal{H}_2t/\hbar}$$
$$= \gamma e^{+it\mathbf{c}_2}e^{-(2\Delta\bar{\omega}+\bar{J})t} + e^{-i\mathbf{b}_2t}\gamma' e^{-(2\Delta\bar{\omega}-\bar{J})t}. \tag{8}$$

Thus we have arrived at a closed form expression for the evolution of the double quantum operators under both $\mathcal{H}_1$ and $\mathcal{H}_2$. However, to proceed further, it is necessary to diagonalize the $3 \times 3$ matrices $\mathbf{b}_2$ and $\mathbf{c}_2$. On denoting the required $3 * 3$ unitary matrices by $\mathcal{U}_b$ and $\mathcal{U}_c$, (8) can be recast as

$$\rho(t) = e^{-i\mathcal{H}t/\hbar}\mathbf{A}_+\mathbf{B}_+e^{+i\mathcal{H}t/\hbar} = \gamma\mathcal{U}_c(\mathcal{U}_c^{-1}e^{+it\mathbf{c}_2}\mathcal{U}_c)\mathcal{U}_c^{-1}e^{-(2\Delta\bar{\omega}+\bar{J})t}$$
$$+ \mathcal{U}_b(\mathcal{U}_b^{-1}e^{-it\mathbf{b}_2}\mathcal{U}_b)\mathcal{U}_b^{-1}\gamma' e^{-(2\Delta\bar{\omega}-\bar{J})t}. \tag{9}$$

From an examination of (9) it is clear that the triply degenerate double quantum frequency $(2\Delta\bar{\omega} + \bar{J})$ of $\mathcal{H}_1$ will split into three frequencies of $\omega(c)_1 - (2\Delta\bar{\omega} + \bar{J})$, $\omega(c)_2 - (2\Delta\bar{\omega} + \bar{J})$, and $\omega(c)_3 - (2\Delta\bar{\omega} + \bar{J})$, where $\omega(c)_1$, $\omega(c)_2$ and $\omega(c)_3$ are the

eigenvalues of $\mathbf{c}_2$. Similarly, the degeneracy of the double quantum frequency of $(2\Delta\bar{\omega} - \bar{J})$ will also be lifted by the eigenvalues of $\mathbf{b}_2$. Thus there will be a maximum of six double quantum frequencies, as shown schematically in the right hand side of Fig. 1. However in practice, the actual number of double quantum frequencies determined experimentally is often lower, being determined by transition matrix elements such as

$$\mathrm{TM} = \langle \mathcal{J}_z = -1/2 | \mathbf{T}_2^{\lambda}(\mathbf{k}) | \mathcal{J}_z = 3/2 \rangle , \tag{10}$$

where there are three distinct, but possibly degenerate, $|\mathcal{J}_z = -1/2\rangle$ eigenfunctions belonging to the $3 \times 3$ $\mathbf{c}_2$ matrix of Table 1.

Finally, we note also that only if $\mathbf{b}_2$ and $\mathbf{c}_2$ are diagonal will the matrices $\gamma$ and $\gamma'$ remain intact and oscillate at a single frequency. In general, the matrices $\alpha$, $\beta$, $\gamma$ and $\alpha'$, $\beta'$, $\gamma'$ will admix as time progresses. That is $\mathbf{A}_+\mathbf{B}_+$ will evolve into $\mathbf{A}_+\mathbf{C}_+$ and $\mathbf{B}_+\mathbf{C}_+$ components and vice versa.

Next, we address the more difficult problem of calculating the evolution of the single quantum operators, say $\mathbf{A}_+$. For these operators their matrix counterparts take the form

$$\mathbf{A}_+ = \begin{array}{c|cccc} & 0 & 1 & 1' & 0' \\ \hline 0 & 0 & \epsilon & 0 & 0 \\ 1 & 0 & 0 & \delta & 0 \\ 1' & 0 & 0 & 0 & \epsilon' \\ 1' & 0 & 0 & 0 & 0 \end{array} \tag{11}$$

Since the precise form of the matrices $\epsilon$, $\delta$, $\epsilon'$, is unimportant for our discussion, we shall not trouble to write them out. After some manipulation, we find

$$\rho_1(t) = e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+ e^{+i\mathcal{H}_1 t/\hbar} = \epsilon e^{-it(a_1 - \mathbf{b}_1)} + e^{-it(\mathbf{c}_1 - d_1)}\epsilon' + e^{-it\mathcal{L}_1}\delta , \tag{12}$$

where $\mathcal{L}_1$ is the Louiville operator

$$\mathcal{L}_1\delta = [\mathcal{H}_1, \delta]_- = \mathbf{b}_1\delta - \delta\mathbf{c}_1 . \tag{13}$$

For $\mathcal{H}_1$, the matrices $\mathbf{b}_1$ and $\mathbf{c}_1$ are diagonal and triply degenerate. Consequently,

$$\mathcal{L}_1\delta = \Delta\bar{\omega}\delta \tag{14}$$

and so

$$\rho_1(t) = e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+ e^{+i\mathcal{H}_1 t/\hbar} = \epsilon e^{-i(\Delta\bar{\omega}+\bar{J})t} + e^{-i(\Delta\bar{\omega}-\bar{J})t}\epsilon' + e^{-i\Delta\bar{\omega}t}\delta . \tag{15}$$

Thus under $\mathcal{H}_1$ the evolution of $\mathbf{A}_+$ is characterized by the three single quantum frequencies $(\Delta\bar{\omega} \pm \bar{J})$ and $\Delta\bar{\omega}$, although these are not observed in practice. To determine the true single quantum NMR frequencies, we must examine the subsequent evolution of $\rho_1(t)$ under $\mathcal{H}_2$. We find

$$\rho(t) = e^{-i\mathcal{H}_2 t/\hbar}\rho_1(t)e^{+i\mathcal{H}_2 t/\hbar}$$
$$= \epsilon e^{+it\mathbf{b}_2}e^{-i(\Delta\bar{\omega}+\bar{J})t} + e^{-it\mathbf{c}_2}\epsilon' e^{-i(\Delta\bar{\omega}-\bar{J})t} + e^{-it\mathcal{L}_2}\delta e^{-i\Delta\bar{\omega}t}, \tag{16}$$

where

$$\mathcal{L}_2\delta = [\mathcal{H}_2, \delta]_- = \mathbf{b}_2\delta - \delta\mathbf{c}_2 . \tag{17}$$

From an examination of the first two terms in (16), it is clear that the NMR signals will be determined by the eigenvalues of say $\mathbf{b}_2$ minus $(\Delta\bar{\omega} + \bar{J})$, etc. However, the calculation of the third term is much more difficult. In summary, therefore, even the use of partitioned algebra does not help us to find simple closed form $\Delta m = \pm 1$ solutions for $ABC$ systems.

## 3. A four spin 1/2 scalar coupled $ABCD$ spin system

For the $ABCD$ four spin 1/2 assembly discussed in paper I, the relevant Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ can be expressed in the partitioned form

$$\mathcal{H}_1/\hbar = \begin{array}{c} \begin{array}{ccccc} 0 & \frac{3}{2} & \frac{5}{2} & \frac{3'}{2} & 0' \end{array} \\ \left[\begin{array}{ccccc} a_1 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{b}_1 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{c}_1 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{d}_1 & 0 \\ 0 & 0 & 0 & 0 & e_1 \end{array}\right] \end{array}, \quad \mathcal{H}_2/\hbar = \begin{array}{c} \begin{array}{ccccc} 0 & \frac{3}{2} & \frac{5}{2} & \frac{3'}{2} & 0' \end{array} \\ \left[\begin{array}{ccccc} 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{b}_2 & 0 & 0 & 0 \\ 0 & 0 & \mathbf{c}_2 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{d}_2 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array}\right] \end{array} \tag{18}$$

where the relevant matrix entries are summarized in Table 4. Here the 16 × 16

Table 3
Unit tensor operators for an $ABC$ coupled spin 1/2 system, with order $Q = \pm 2$.

| | |
|---|---|
| $\hat{\mathbf{T}}^3_{\pm 3}(\underline{\mathbf{k}}_\alpha) = \mp\mathbf{A}_\pm\mathbf{B}_\pm\mathbf{C}_\pm$ | $\hat{\mathbf{T}}^2_{\pm 2}(\underline{\mathbf{k}}_\gamma) = \frac{1}{\sqrt{2}}\mathbf{B}_\pm\mathbf{C}_\pm$ |
| $\hat{\mathbf{T}}^3_{\pm 2}(\underline{\mathbf{k}}_\alpha) = (\frac{2}{3})^{\frac{1}{2}}[\mathbf{A}_z\mathbf{B}_\pm\mathbf{C}_\pm + \mathbf{A}_\pm\mathbf{B}_z\mathbf{C}_\pm + \mathbf{A}_\pm\mathbf{B}_\pm\mathbf{C}_z]$ | $\hat{\mathbf{T}}^2_{\pm 2}(\underline{\mathbf{k}}_\delta) = \frac{1}{\sqrt{2}}\mathbf{A}_\pm\mathbf{C}_\pm$ |
| $\hat{\mathbf{T}}^2_{\pm 2}(\underline{\mathbf{k}}_\alpha) = \mp\frac{1}{\sqrt{3}}[\mathbf{A}_z\mathbf{B}_\pm\mathbf{C}_\pm + \mathbf{A}_\pm\mathbf{B}_z\mathbf{C}_\pm - 2\mathbf{A}_\pm\mathbf{B}_\pm\mathbf{C}_z]$ | $\hat{\mathbf{T}}^2_{\pm 2}(\underline{\mathbf{k}}_\epsilon) = \frac{1}{\sqrt{2}}\mathbf{A}_\pm\mathbf{B}_\pm$ |
| $\hat{\mathbf{T}}^2_{\pm 2}(\underline{\mathbf{k}}_\beta) = \mp[\mathbf{A}_z\mathbf{B}_\pm\mathbf{C}_\pm - \mathbf{A}_\pm\mathbf{B}_z\mathbf{C}_\pm]$ | |
| Three coupled spin 1/2 tensor operators | Two coupled spin 1/2 tensor operators |

*Legend coupling schemes:*

$\underline{\mathbf{k}}_\alpha : \mathbf{k}_A + \mathbf{k}_B = \mathbf{K}'(=2); \quad \mathbf{K}' + \mathbf{k}_C = \mathbf{K}(=1,2,3)$
$\underline{\mathbf{k}}_\beta : \mathbf{k}_A + \mathbf{k}_B = \mathbf{K}'(=1); \quad \mathbf{K}' + \mathbf{k}_C = \mathbf{K}(=0,1,2)$
$\underline{\mathbf{k}}_\gamma : \mathbf{k}_A(=0) + \mathbf{k}_B = \mathbf{K}'(=1); \quad \mathbf{K}' + \mathbf{k}_C(=1) = \mathbf{K}(=0,1,2)$
$\underline{\mathbf{k}}_\delta : \mathbf{k}_A + \mathbf{k}_B(=0) = \mathbf{K}'(=1); \quad \mathbf{K}' + \mathbf{k}_C(=1) = \mathbf{K}(=0,1,2)$
$\underline{\mathbf{k}}_\epsilon : \mathbf{k}_A + \mathbf{k}_B = \mathbf{K}'(=2); \quad \mathbf{K}' + \mathbf{k}_C(=0) = \mathbf{K}(=2)$

Table 4
The matrices, $a_1$, $\mathbf{b}_1$, $\mathbf{c}_1$, $\mathbf{d}_1$, $e_1$, $\mathbf{b}_2$, $\mathbf{c}_2$, and $\mathbf{d}_2$ for eq. (18). **I** is the unit matrix.

$a_1 = (2\Delta\bar{\omega} + \frac{3}{2}\bar{J})$; $\quad e_1 = (-2\Delta\bar{\omega} + \frac{3}{2}\bar{J})$
$\mathbf{b}_1 = \Delta\bar{\omega}\mathbf{I}(4\times 4)$; $\quad \mathbf{d}_1 = -\Delta\bar{\omega}\mathbf{I}(4\times 4)$
$\mathbf{c}_1 = -\frac{1}{2}\bar{J}\mathbf{I}(6\times 6)$

$$\mathbf{b}_2 = \begin{bmatrix} a+\Delta\omega_1 & J'_{CD} & J'_{BD} & J'_{AD} \\ J'_{CD} & b+\Delta\omega_2 & J'_{BC} & J'_{AC} \\ J'_{BD} & J'_{BC} & d+\Delta\omega_4 & J'_{AB} \\ J'_{AD} & J'_{AC} & J'_{AB} & g+\Delta\omega_7 \end{bmatrix}; \quad \mathbf{d}_2 = \begin{bmatrix} a-\Delta\omega_1 & J'_{CD} & J'_{BD} & J'_{AD} \\ J'_{CD} & b-\Delta\omega_2 & J'_{BC} & J'_{AC} \\ J'_{BD} & J'_{BC} & d-\Delta\omega_4 & J'_{AB} \\ J'_{AD} & J'_{AC} & J'_{AB} & g-\Delta\omega_7 \end{bmatrix}$$

$$\mathbf{c}_2 = \begin{bmatrix} c+\Delta\omega_3 & J'_{BC} & J'_{BD} & 0 & J'_{AD} & J'_{AC} \\ J'_{BC} & e+\Delta\omega_5 & J'_{CD} & J'_{AD} & 0 & J'_{AB} \\ J'_{BD} & J'_{CD} & f+\Delta\omega_6 & J'_{AC} & J'_{AB} & 0 \\ 0 & J'_{AD} & J'_{AC} & c-\Delta\omega_3 & J'_{BC} & J'_{BD} \\ J'_{AD} & 0 & J'_{AB} & J'_{BC} & e-\Delta\omega_5 & J'_{CD} \\ J'_{AC} & J'_{AB} & 0 & J'_{BD} & J'_{CD} & f-\Delta\omega_6 \end{bmatrix}$$

matrices for $\mathcal{H}_1$ and $\mathcal{H}_2$ are labelled according to $\mathcal{J}_z = \pm 2$ ($1\times 1$ matrix), $\mathcal{J}_z = \pm 1$ (two $4\times 4$ matrices), and $\mathcal{J}_z = \pm 0$ (one $6\times 6$ matrix), which suggests the abbreviated labelling scheme $\{0, 3/2, 5/2, 3/2', 0'\}$. Once again, $\mathcal{H}_1$ is diagonal and presents no real difficulties. On the other hand $\mathcal{H}_2$ contains both diagonal and off-diagonal terms. Note that (i) the definitions of the coefficients $a$, $b$, $c$, etc., differ from those used for the $ABC$ system, as stated in [1], and (ii) the first and last rows and the first and last columns in the $16\times 16$ matrix of $\mathcal{H}_2$ are zero. Thus $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+\mathbf{D}_+$ and $\mathbf{A}_-\mathbf{B}_-\mathbf{C}_-\mathbf{D}_-$ are constants of the motion under $\mathcal{H}_2$.

We are now in a position to examine the evolution of, say, the triple quantum term $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$ whose matrices are summarized in Table 5. Proceeding in exactly the same fashion as for the $ABC$ spin system, the evolution of the $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$ triple quantum operator under $\mathcal{H}_1$ is given by

$$\begin{aligned} e^{-i\mathcal{H}_1 t/\hbar}\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+ e^{+i\mathcal{H}_1 t/\hbar} &= \alpha e^{-it(a_1-\mathbf{d}_1)} + e^{-it(\mathbf{b}_1-e_1)}\alpha' \\ &= \alpha e^{-it(3\Delta\bar{\omega}+3\bar{J}/2)} + e^{-it(3\Delta\bar{\omega}-3\bar{J}/2)}\alpha', \end{aligned} \tag{19}$$

where the matrices $\alpha$ and $\alpha'$ are defined in Table 5. Consequently, the evolution of the triple quantum operator under the total Hamiltonian $\mathcal{H}$ is given by

$$\begin{aligned} \rho(t) &= e^{-i\mathcal{H}t/\hbar}\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+ e^{+i\mathcal{H}t/\hbar} \\ &= \alpha e^{+it\mathbf{d}_2} e^{-it(3\Delta\bar{\omega}+3\bar{J}/2)} + e^{-it(3\Delta\bar{\omega}-3\bar{J}/2)} e^{-it\mathbf{b}_2}\alpha'. \end{aligned} \tag{20}$$

Note that the $6\times 6$ matrices $\mathbf{c}_1$ and $\mathbf{c}_2$ play no role in determining the evolution of the triple quantum states. In fact to determine the beating frequencies associated with the evolution of any triple quantum state available to the four spin 1/2 system it is only really necessary to diagonalize say the $4\times 4$ matrix $\mathbf{b}_2$, given that $\mathbf{b}_2$ and

Table 5
The triple quantum operators $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$, etc. The numbers outside the matrices refer to the original labels of (22) of [1].

$$\begin{array}{lcccccc} & & 15 & 14 & 12 & 8 & \\ \langle 0|\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+|\tfrac{3'}{2}\rangle = 1 & & 1 & 0 & 0 & 0 & = \alpha \\ \langle 0|\mathbf{A}_+\mathbf{B}_+\mathbf{D}_+|\tfrac{3'}{2}\rangle = 1 & & 0 & 1 & 0 & 0 & = \beta \\ \langle 0|\mathbf{A}_+\mathbf{C}_+\mathbf{D}_+|\tfrac{3'}{2}\rangle = 1 & & 0 & 0 & 1 & 0 & = \gamma \\ \langle 0|\mathbf{B}_+\mathbf{C}_+\mathbf{D}_+|\tfrac{3'}{2}\rangle = 1 & & 0 & 0 & 0 & 1 & = \alpha \end{array}$$

$$\langle \tfrac{3}{2}|\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+|0'\rangle = \begin{array}{cc} & 16 \\ 2 & 1 \\ 3 & 0 \\ 5 & 0 \\ 9 & 0 \end{array} = \alpha'; \quad \langle \tfrac{3}{2}|\mathbf{A}_+\mathbf{B}_+\mathbf{D}_+|0'\rangle = \begin{array}{cc} & 16 \\ 2 & 0 \\ 3 & 1 \\ 5 & 0 \\ 9 & 0 \end{array} = \beta'$$

$$\langle \tfrac{3}{2}|\mathbf{A}_+\mathbf{C}_+\mathbf{D}_+|0'\rangle = \begin{array}{cc} 2 & 0 \\ 3 & 0 \\ 5 & 1 \\ 9 & 0 \end{array} = \gamma'; \quad \langle \tfrac{3}{2}|\mathbf{B}_+\mathbf{C}_+\mathbf{D}_+|0'\rangle = \begin{array}{cc} 2 & 0 \\ 3 & 0 \\ 5 & 0 \\ 9 & 1 \end{array} = \delta'$$

$\mathbf{d}_2$ are simply related. Thus a maximum of eight beating frequencies is possible, although the actual number will be reduced by symmetry considerations.

Clearly, the methods described in this and the preceding paper can be extended to higher numbers of connected spins. For example, for $n$-coupled spin 1/2 nuclei, the $n$th order multiple quantum state is a constant of the motion under $\mathcal{H}_2$ and evolves at a frequency of $n\Delta\bar{\omega}$ under $\mathcal{H}_1$. Further, for $n$-coupled spin 1/2 nuclei it is only necessary to diagonalize at most two $n \times n$ matrices to determine the beating frequencies associated with the $Q = \pm K_{\max} \mp 1$ multipolar states.

## 4. Conclusions

In this paper, the spin dynamics of high order multipolar states with $Q = \pm K_{\max}$ and $Q = \pm K_{\max} \mp 1$ for multiply connected spin 1/2 nuclei have been examined using (i) the fact that $\mathcal{J}_z$ is a good quantum number, and (ii) the theory of partitioned matrices. In particular, it has been shown that to describe the spin dynamics of high-order multipolar states with $Q = \pm K_{\max} \mp 1$, it is only necessary to diagonalize at most two $n \times n$ matrices. Since the full Hamiltonian matrix has dimensions of $2^n \times 2^n$, this constitutes a considerable saving in mathematical labour.

Finally, a word of caution has been given concerning the weak-coupling approximation, particularly for homonuclear spin systems. In this approximation, the original single spin Zeeman labels are still good quantum labels. However, it is

apparent, from an examination of the matrices $\mathbf{b}_2$, $\mathbf{c}_2$ in Table 1, and $\mathbf{b}_2$, $\mathbf{c}_2$, and $\mathbf{d}_2$ in Table 4, that considerable admixing will take place between states with the same $\mathcal{J}_z$ $(= A_z + B_z + C_z + \ldots)$ values. Thus conclusions based on the weak coupling limit should be viewed with caution, not only in the limit $\Delta\omega \to 0$, but also in the presence of degeneracies.

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