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

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By choosing a suitable linear combination of the constants of the motion $\mathcal{H}_1$, it is shown that the calculation of the density matrix $\rho(t)$ can be simplified by subdividing the Hamiltonian $\mathcal{H}$ into $(\mathcal{H}_1 + \mathcal{H}_2)$. In particular, this technique can be used to obtain closed form solutions for the eigenfunctions and eigenvalues of spin 1/2 *ABC* and *XBCD* spin systems, evolving in the presence of Zeeman offsets, scalar coupling and dipolar interactions. In general, the eigenvalues and eigenvalues of $\mathcal{H}_1$ are very transparent, while those of $\mathcal{H}_2$ require more effort. Nevertheless, simplifications can be made. Firstly, the effective size of the Hamiltonian matrix $\mathcal{H}_2$ which needs to be considered, is reduced from $N \times N$ to at least $(N-2) \times (N-2)$, while for *XBC*... systems it is reduced to $(N-4) \times (N-4)$. Secondly, the highest rank and highest/lowest order tensor operators available to the spin ensemble are constants of the motion under $\mathcal{H}_2$. Finally, by exploiting the fact that $\mathcal{J}_z$ is a good quantum number, it is possible to block-diagonalize the $\mathcal{H}_2$ matrix into no more than 3×3 matrices.

1. Introduction

The complexity of the mathematics required to describe the evolution of nuclear ensembles, increases rapidly with the number of interacting nuclei [1–5]. Thus it is helpful to seek ways of simplifying the algebra required for coupled spin 1/2 nuclei evolving in the presence of Zeeman offsets, dipole-dipole interactions, and scalar coupling. A step in this direction has been made by [6]. In a paper on the product operator description of *AB* and *ABX* spin systems, it was shown that the calculation of the time dependent density matrix $\rho(t)$ can be simplified, by subdividing the Hamiltonian into the form $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, where $\mathcal{H}_1$ and $\mathcal{H}_2$ commute. In such cases, the time evolution of the density matrix can be factorised as

$$\begin{aligned}\rho(t) &= e^{-i\mathcal{H}t/\hbar}\rho(0)e^{+i\mathcal{H}t/\hbar} \\ &= e^{-i\mathcal{H}_2 t/\hbar}\left[e^{-i\mathcal{H}_1 t/\hbar}\rho(0)e^{+i\mathcal{H}_1 t/\hbar}\right]e^{+i\mathcal{H}_2 t/\hbar}\,, \qquad (1)\end{aligned}$$

enabling the calculation of the density matrix $\rho(t)$ to be carried out in two separate steps rather than one. In practice, this approach is useful because (i) it allows the identification of "constants of the motion", under $\mathcal{H}_1$ and $\mathcal{H}_2$ taken separately, and (ii) the eigenvalues and eigenfunctions of $\mathcal{H}_1$ and $\mathcal{H}_2$ are often less complicated than those of $\mathcal{H}$.

In this paper, an optimal subdivision of $\mathcal{H}$ into $\mathcal{H}_1$ and $\mathcal{H}_2$, for *ABC*, *XBC*, *ABCD*, and *XBCD*, etc., spin 1/2 spin systems is presented and discussed. In essence, $\mathcal{H}_1$ is chosen to be a suitable linear combination of the constants of the motion of the Hamiltonian $\mathcal{H}$. It is demonstrated that (i) in the Zeeman representation, $\mathcal{H}_1$ is pure diagonal, and (ii) the effective size of the non-diagonal $\mathcal{H}_2$ matrix is reduced from $N \times N$ to at least $(N-2) \times (N-2)$. In addition, it is shown that even the $(N-2) \times (N-2)$ $\mathcal{H}_2$ matrix can be block diagonalized into still smaller sub-matrices, using the fact that $\mathcal{J}_z$ $(= A_z + B_z + C_z + \dots)$ is a good quantum number.

The structure of papers I and II is as follows. In this paper, the emphasis is placed on (i) the optimal subdivision of $\mathcal{H}$ into $\mathcal{H}_1 + \mathcal{H}_2$, (ii) identification of constants of the motion, and (iii) block-diagonalization. In the following paper II, it is shown that it is possible to determine the evolution of high order multipolar states, without the need to diagonalize the full Hamiltonian $\mathcal{H}$. Both papers I and II can be seen as extensions of the work initiated in [6], to deal with higher numbers of multiply connected spin-1/2 systems.

2. General considerations

To obtain explicit forms for the time dependence of the density matrix $\rho(t)$ of (1), it is necessary to choose a suitable basis set of operators [7]. In practice, there are several sets of operators that can be used for coupled spin-systems: Cartesian product operators [8], concatenated tensor operators [9], and unit spherical tensor operators [10]. For our purposes, we shall use the concatenated set of [9,10], denoted by $\hat{\mathbf{T}}^{\lambda}_{Q}(\mathbf{k})$. Here λ and Q denote the rank and order of the operator, while $\mathbf{k}$ represents the spin-coupling scheme. Thus the term inside the square brackets of (1), can be rewritten in the form

$$\rho_1(t) = e^{-i\mathcal{H}_1 t/\hbar}\rho(0)e^{+i\mathcal{H}_1 t/\hbar} = \sum_{\lambda Q}\sum_{\mathbf{k}} \rho^{\lambda}_{Q}(\mathbf{k}, t)\hat{\mathbf{T}}^{\lambda}_{Q}(\mathbf{k})\,. \tag{2}$$

In the energy representation, it is easily shown that the time dependent Fano coefficients [7] $\rho^{\lambda}_{Q}(\mathbf{k}, t)$ are given by

$$\begin{aligned}\rho^{\lambda}_{Q}(\mathbf{k}, t) &= \mathrm{Tr}\left[(\hat{\mathbf{T}}^{\lambda}_{Q}(\mathbf{k}))^{\dagger}\rho_1(t)\right] \\ &= \sum_{nm}\langle n|(\hat{\mathbf{T}}^{\lambda}_{Q}(\bar{\mathbf{k}}))^{\dagger}|m\rangle\langle m|\rho(0)|n\rangle e^{-i(E_n - E_m)t/\hbar}\,.\end{aligned} \tag{3}$$

Consequently, given the eigenvalues and eigenfunctions of $\mathcal{H}_1$, it is a relatively straightforward matter to determine the Fano coefficients and so arrive at an explicit form for $\rho_1(t)$. Once this has been done, the full density matrix $\rho(t)$ can be obtained, this time using the eigenvalues and eigenfunctions of $\mathcal{H}_2$:

$$\rho(t) = e^{-i\mathcal{H}_2 t/\hbar}\rho_1(t)e^{+i\mathcal{H}_2 t/\hbar} . \tag{4}$$

Thus the key to the calculation of the density matrix $\rho(t)$ lies in the determination of eigenvalues and eigenvectors of $\mathcal{H}_1$ and $\mathcal{H}_2$.

3. A three spin 1/2 scalar coupled *ABC* spin system

First, we observe that if $[\mathcal{H}_1, \mathcal{H}_2]_- = 0$, it follows that both $[\mathcal{H}, \mathcal{H}_1]_- = 0$ and $[\mathcal{H}, \mathcal{H}_2]_- = 0$. Thus in order to construct a reasonable choice for say $\mathcal{H}_1$ we seek the constants of the motion for the Hamiltonian $\mathcal{H}$.

Consider a general *ABC* scalar coupled spin 1/2 spin system. In the decoupled representation, the Hamiltonian can be written in the form

$$\mathcal{H} = \hbar[\Delta\omega_A \mathbf{A}_z + \Delta\omega_B \mathbf{B}_z + \Delta\omega_C \mathbf{C}_z] + J_{AB}\mathbf{A}\cdot\mathbf{B} + J_{AC}\mathbf{A}\cdot\mathbf{C} + J_{BC}\mathbf{B}\cdot\mathbf{C} . \tag{5}$$

For such a Hamiltonian, it is easily shown that

$$[\mathbf{A}_z + \mathbf{B}_z + \mathbf{C}_z, \mathcal{H}]_- = [\mathcal{J}_z, \mathcal{H}]_- = 0 , \tag{6}$$

i.e. the total projection of the angular momentum along the z-axis $\mathcal{J}_z$ is conserved. Further, given (6) it is easy to show that $\mathcal{J}_z^2$ is also a constant of the motion. Consequently,

$$\begin{aligned} [\mathcal{J}_z^2, \mathcal{H}]_- &= \left[(\mathbf{A}_z + \mathbf{B}_z + \mathbf{C}_z)^2, \mathcal{H}\right]_- \\ &= [(\mathbf{A}_z\mathbf{B}_z + \mathbf{A}_z\mathbf{C}_z + \mathbf{B}_z\mathbf{C}_z), \mathcal{H}]_- = 0 , \end{aligned} \tag{7}$$

where we have made use of the fact that $(\mathbf{A}_z^2 + \mathbf{B}_z^2 + \mathbf{C}_z^2) = 3/4$ for spin 1/2 nuclei. Thus we have now identified two constants of the motion (6) and (7). This suggests therefore that we set

$$\mathcal{H}_1 = \hbar[\Delta\bar{\omega}(\mathbf{A}_z + \mathbf{B}_z + \mathbf{C}_z)] + \bar{J}(\mathbf{A}_z\mathbf{B}_z + \mathbf{A}_z\mathbf{C}_z + \mathbf{B}_z\mathbf{C}_z) , \tag{8}$$

where (i)

$$\Delta\bar{\omega} = \tfrac{1}{3}[\Delta\omega_A + \Delta\omega_B + \Delta\omega_C] \tag{9}$$

and (ii)

$$\bar{J} = \tfrac{1}{3}[J_{AB} + J_{AC} + J_{BC}] . \tag{10}$$

With this choice of $\mathcal{H}_1$ therefore

$$\begin{aligned} \mathcal{H}_2 = \hbar[&(\Delta\omega_A - \Delta\bar{\omega})\mathbf{A}_z + (\Delta\omega_B - \Delta\bar{\omega})\mathbf{B}_z + (\Delta\omega_C - \Delta\bar{\omega})\mathbf{C}_z] \\ &+ (J_{AB}\mathbf{A}\cdot\mathbf{B} - \bar{J}\mathbf{A}_z\mathbf{B}_z) + (J_{AC}\mathbf{A}\cdot\mathbf{C} - \bar{J}\mathbf{A}_z\mathbf{C}_z) + (J_{BC}\mathbf{B}\cdot\mathbf{C} - \bar{J}\mathbf{B}_z\mathbf{C}_z) . \end{aligned} \tag{11}$$

Note that in choosing $\mathcal{H}_1$ we have been driven by the idea that $\mathcal{H}_1$ should contain the dominant terms in the Hamiltonian: i.e., $\mathcal{H}_1 > \mathcal{H}_2$.

In the Zeeman representation $\mathcal{H}_1$ is diagonal, so the calculation of the density matrix $\rho_1(t)$ inside the square brackets of (1), presents no difficulties. On the other hand, the calculation of the eigenfunctions and the eigenvalues of $\mathcal{H}_2$ is more complicated. Using the labelling scheme and definitions set out in Table 1, we find

$$\mathcal{H}_2/\hbar = \begin{array}{cccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & a+\Delta\omega_1 & J'_{BC} & 0 & J'_{AC} & 0 & 0 & 0 \\ 0 & J'_{BC} & b+\Delta\omega_2 & 0 & J'_{AB} & 0 & 0 & 0 \\ 0 & 0 & 0 & c-\Delta\omega_3 & 0 & J'_{AB} & J'_{AC} & 0 \\ 0 & J'_{AC} & J'_{AB} & 0 & c+\Delta\omega_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & J'_{AB} & 0 & b-\Delta\omega_2 & J'_{BC} & 0 \\ 0 & 0 & 0 & J'_{AC} & 0 & J'_{BC} & a-\Delta\omega_1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline \end{array} \tag{12}$$

Note that the first and last entries along the diagonal in $\mathcal{H}_2$ are zero. For such entries, the projections of A_z, B_z, and C_z are all identical, and so both the diagonal Zeeman and scalar coupling terms vanish identically. This is also true of all the entries in the first and last rows, and the first and last columns, since entries in these positions would correspond to spin-flips which do not conserve $\mathcal{J}_z$. Thus two eigenvalues of $\mathcal{H}_2$ are identically equal to zero, and the effective size of the Hamiltonian has been reduced from 8×8 to 6×6. This observation is readily generalized to *ABCD*, *ABCDE*, etc., spin 1/2 systems. If the dimensions of $\mathcal{H}$ are $N \times N$, the effective size of $\mathcal{H}_2$ is reduced to $(N-2) \times (N-2)$, which allows us to draw a general conclusion. The highest rank tensor K with the highest/lowest order $Q = \pm K$ is a constant of the motion under $\mathcal{H}_2$. For the *ABC* spin system, this would correspond to the operators $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$ and $\mathbf{A}_-\mathbf{B}_-\mathbf{C}_-$, which have sole entries in the matrix positions (1,8) and (8,1), respectively.

Further progress can be made by relabeling the rows and columns of (12), to

Table 1
Labelling scheme and definitions used in $\mathcal{H}_2$ of eq. (12) for the *ABC* spin system.

$a = \frac{1}{2}[J_{AB} - \bar{J}]/\hbar;\quad b = \frac{1}{2}[J_{AC} - \bar{J}]/\hbar;\quad c = \frac{1}{2}[J_{BC} - \bar{J}]/\hbar$

$\bar{J} = \frac{1}{3}[J_{AB} + J_{AC} + J_{BC}];\quad J' = J/(2\hbar)$

$a + b + c = 0$

$\Delta\omega_1 = (\Delta\bar{\omega} - \Delta\omega_C);\quad \Delta\omega_2 = (\Delta\bar{\omega} - \Delta\omega_B);\quad \Delta\omega_3 = (\Delta\bar{\omega} - \Delta\omega_A)$

$\Delta\bar{\omega} = \frac{1}{3}[\Delta\omega_A + \Delta\omega_B + \Delta\omega_C];\quad \Delta\omega_1 + \Delta\omega_2 + \Delta\omega_3 = 0$

Labelling scheme: $|A_z B_z C_z\rangle$, i.e.

$|1\rangle = |+\frac{1}{2}\ +\frac{1}{2}\ +\frac{1}{2}\rangle,\quad |2\rangle = |+\frac{1}{2}\ +\frac{1}{2}\ -\frac{1}{2}\rangle,\quad |3\rangle = |+\frac{1}{2}\ -\frac{1}{2}\ +\frac{1}{2}\rangle$, etc.

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highlight the fact that $\mathcal{J}_z$ is a good quantum number. Thus (12) is transformed to

$$\begin{array}{r|cccccccc|}
\mathcal{J}_z = & 3/2 & \multicolumn{3}{c}{1/2} & \multicolumn{3}{c}{-1/2} & -3/2 \\
 & 1 & 2 & 3 & 5 & 7 & 6 & 4 & 8 \\
\hline
 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 & 0 & a+\Delta\omega_1 & J'_{BC} & J'_{AC} & 0 & 0 & 0 & 0 \\
 & 0 & J'_{BC} & b+\Delta\omega_2 & J'_{AB} & 0 & 0 & 0 & 0 \\
\mathcal{H}_2/\hbar = & 0 & J'_{AC} & J'_{AB} & c+\Delta\omega_3 & 0 & 0 & 0 & 0 \\
 & 0 & 0 & 0 & 0 & a-\Delta\omega_1 & J'_{BC} & J'_{AC} & 0 \\
 & 0 & 0 & 0 & 0 & J'_{BC} & b-\Delta\omega_2 & J'_{AB} & 0 \\
 & 0 & 0 & 0 & 0 & J'_{AC} & J'_{AB} & c-\Delta\omega_3 & 0 \\
 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
\end{array} \tag{13}$$

which is now block diagonal with just two 3×3 matrices down the diagonal. Note that the two 3×3 matrices in (13) are simply related to each other in that the Zeeman terms change sign on going from $\mathcal{J}_z = +1/2$ to $-1/2$.

We are now in a position to make two more observations. One, since $\mathcal{H}_2$ is block diagonal in $\mathcal{J}_z$, evolution under $\mathcal{H}_2$ (and $\mathcal{H}_1$) cannot change the order Q of a given tensor operator $\hat{\mathbf{T}}^K_Q(\mathbf{k})$. For example, operators with $Q = \pm 2$ can only evolve between $\hat{\mathbf{T}}^3_{\pm 2}(\mathbf{k})$ and $\hat{\mathbf{T}}^2_{\pm 2}(\mathbf{k})$ multipolar states. Two, since the dimensions of the largest matrix appearing in (13) is only 3×3, closed form expressions for the eigenvalues and eigenfunctions of $\mathcal{H}_2$ are guaranteed. Note also that the trace of each of the two 3×3 matrices appearing in (13) is zero. In general, the 3×3 matrices take the form

$$\mathbf{M} = \begin{bmatrix} \alpha & A & B \\ A & \beta & C \\ B & C & -(\alpha+\beta) \end{bmatrix}, \tag{14}$$

which possesses the characteristic equation

$$\lambda^3 - \gamma\lambda + \epsilon = 0, \tag{15}$$

where

$$\gamma = [(A^2 + B^2 + C^2) + (\alpha^2 + \alpha\beta + \beta^2)],$$

$$\epsilon = [(\alpha C^2 + \beta B^2) + (\alpha + \beta)(\alpha\beta - A^2) - 2ABC]. \tag{16}$$

Thus standard methods can be used to obtain the eigenvalues, and hence the eigenvectors. Of course, further simplifications can be made for AB^2 type spin systems, and a simple example is discussed below in the section 7.

Finally, we remark that the above treatment can be used to discuss the ABX system. This can be achieved by setting C equal to X and the off-diagonal terms J'_{AC} and J'_{BC} in (12) equal to zero. For such systems therefore it is only necessary to diagonalize two 2 × 2 matrices. However, as noted by [6] there is a better way of tackling the ABX spin problem.

The ABX Hamiltonian can be divided into $\mathcal{H}_1$ and $\mathcal{H}_2$ where (i)

$$\mathcal{H}_1 = \hbar[\Delta\bar{\omega}_{AB}(\mathbf{A}_z + \mathbf{B}_z) + \Delta\omega_X\mathbf{X}_z] + J_{AB}\mathbf{A}_z\mathbf{B}_z + \bar{J}_X(\mathbf{A}_z + \mathbf{B}_z)\mathbf{X}_z\,, \tag{17}$$

(ii)

$$\begin{aligned}\mathcal{H}_2 = {} & \hbar[(\Delta\bar{\omega}_A - \Delta\omega_{AB})\mathbf{A}_z + (\Delta\omega_B - \Delta\bar{\omega}_{AB})\mathbf{B}_z] \\ & + J_{AB}(\mathbf{A}\cdot\mathbf{B} - \mathbf{A}_z\mathbf{B}_z) + \delta\bar{J}_X(\mathbf{A}_z - \mathbf{B}_z)\mathbf{X}_z\end{aligned} \tag{18}$$

and (iii)

$$\bar{J}_x = \tfrac{1}{2}(J_{AX} + J_{BX})\,; \quad \delta\bar{J}_x = \tfrac{1}{2}(J_{AX} - J_{BX})\,; \quad \Delta\bar{\omega}_{AB} = \tfrac{1}{2}[\Delta\omega_A + \Delta\omega_B]\,. \tag{19}$$

Note that in writing (17) and (18), the off-diagonal terms in $\mathbf{A}\cdot\mathbf{X}$ and $\mathbf{B}\cdot\mathbf{X}$ have been dropped because such flip-flop terms do not conserve energy and are therefore strongly suppressed. With this approximation therefore, both $(A_z + B_z)$ and X_z, taken separately, are good quantum numbers. In practice, of course, both approaches must lead ultimately to the same results. However, for the ABX spin system, the sub-division of (17) and (18) is optimal because $\mathcal{H}_1$ more closely reflects the dominant terms in the ABX Hamiltonian.

4. A four spin 1/2 scalar coupled *ABCD* spin system

Having made reasonable progress with the three spin 1/2 problem, it is natural to enquire how much further can we go. For the $ABCD$ four spin assembly, the relevant $\mathcal{H}$ and $\mathcal{H}_1$ are given by

$$\begin{aligned}\mathcal{H} = {} & \hbar[\Delta\omega_A\mathbf{A}_z + \Delta\omega_B\mathbf{B}_z + \Delta\omega_C\mathbf{C}_z + \Delta\omega_D\mathbf{D}_z] \\ & + (J_{AB}\mathbf{A}\cdot\mathbf{B} + J_{AC}\mathbf{A}\cdot\mathbf{C} + J_{AD}\mathbf{A}\cdot\mathbf{D} + J_{BC}\mathbf{B}\cdot\mathbf{C} + J_{BD}\mathbf{B}\cdot\mathbf{D} + J_{CD}\mathbf{C}\cdot\mathbf{D})\end{aligned} \tag{20}$$

and

$$\begin{aligned}\mathcal{H}_1 = {} & \hbar[\Delta\bar{\omega}(\mathbf{A}_z + \mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z)] \\ & + \bar{J}(\mathbf{A}_z\mathbf{B}_z + \mathbf{A}_z\mathbf{C}_z + \mathbf{A}_z\mathbf{D}_z + \mathbf{B}_z\mathbf{C}_z + \mathbf{B}_z\mathbf{D}_z + \mathbf{C}_z\mathbf{D}_z)\,.\end{aligned} \tag{21}$$

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. In block diagonal form we find

$$\mathcal{H}_2/\hbar = \overbrace{\begin{array}{|cccc|} \multicolumn{4}{c}{\begin{array}{cccc} 2 & 3 & 5 & 9 \end{array}} \\ \hline a+\Delta\omega_1 & J'_{CD} & J'_{BD} & J'_{AD} \\ J'_{CD} & b+\Delta\omega_2 & J'_{BC} & J'_{AC} \\ J'_{BD} & J'_{BC} & d+\Delta\omega_4 & J'_{AB} \\ J'_{AD} & J'_{AC} & J'_{AB} & g+\Delta\omega_7 \\ \hline \end{array}}^{\mathcal{J}_z = 1}$$

$$\oplus \overbrace{\begin{array}{|cccc|} \multicolumn{4}{c}{\begin{array}{cccc} 15 & 14 & 12 & 8 \end{array}} \\ \hline a-\Delta\omega_1 & J'_{CD} & J'_{BD} & J'_{AD} \\ J'_{CD} & b-\Delta\omega_2 & J'_{BC} & J'_{AC} \\ J'_{BD} & J'_{BC} & d-\Delta\omega_4 & J'_{AB} \\ J'_{AD} & J'_{AC} & J'_{AB} & g-\Delta\omega_7 \\ \hline \end{array}}^{\mathcal{J}_z = -1}$$

$$\oplus \overbrace{\begin{array}{|cccccc|} \multicolumn{6}{c}{\begin{array}{cccccc} 4 & 6 & 7 & 13 & 11 & 10 \end{array}} \\ \hline c+\Delta\omega_3 & J'_{BC} & J'_{BD} & 0 & J'_{AD} & J'_{AC} \\ J'_{BC} & e+\Delta\omega_5 & J'_{CD} & J'_{AD} & 0 & J'_{AB} \\ J'_{BD} & J'_{CD} & f+\Delta\omega_6 & J'_{AC} & J'_{AB} & 0 \\ 0 & J'_{AD} & J'_{AC} & c-\Delta\omega_3 & J'_{BC} & J'_{BD} \\ J'_{AD} & 0 & J'_{AB} & J'_{BC} & e-\Delta\omega_5 & J'_{CD} \\ J'_{AC} & J'_{AB} & 0 & J'_{BD} & J'_{CD} & f-\Delta\omega_6 \\ \hline \end{array}}^{\mathcal{J}_z = 0} \qquad (22)$$

Thus $\mathcal{H}_2$ is block diagonal in $\mathcal{J}_z$ consisting of two 4×4, one 6×6, and two null 1×1 matrices $\mathcal{J}_z = \pm 2$ (not shown). The definitions of the terms a, b, c, etc., and symmetries, are summarized in Table 2. Note that the definitions of the coefficients a, b, c etc., for the *ABCD* spin system (Table 2) differ from those of the *ABC* spin system (Table 1).

Clearly, this method can be extended to deal with higher numbers of connected spins. For example, for five spins the $(N-2) \times (N-2)$ Hamiltonian matrix $\mathcal{H}_2$ is reduced to two 5×5 and two 10×10 matrices, while for a six-spin system, $\mathcal{H}_2$ is reduced to two 6×6, two 15×15, and one 20×20 matrices. It is obvious therefore that the required mathematics increases steeply as more spins are added to the nuclear ensemble. In fact, for spins in excess of say 20, one is forced to resort to sta-

Table 2
Definitions and symmetries for $\mathcal{H}_2$ of eq. (22) for the *ABCD* spin system.

$$a\hbar = -\tfrac{3}{2}\bar{J} + \tfrac{1}{2}[J_{AB} + J_{AC} + J_{BC}]; \quad b\hbar = -\tfrac{3}{2}\bar{J} + \tfrac{1}{2}[J_{AB} + J_{AD} + J_{BD}]$$

$$c\hbar = -\bar{J} + \tfrac{1}{2}[J_{AB} + J_{CD}]; \quad d\hbar = -\tfrac{3}{2}\bar{J} + \tfrac{1}{2}[J_{AC} + J_{AD} + J_{CD}]$$

$$e\hbar = -\bar{J} + \tfrac{1}{2}[J_{AC} + J_{BD}]; \quad f\hbar = -\bar{J} + \tfrac{1}{2}[J_{AD} + J_{BC}]$$

$$g\hbar = -\tfrac{3}{2}\bar{J} + \tfrac{1}{2}[J_{BC} + J_{BD} + J_{CD}]$$

$$\bar{J} = \tfrac{1}{6}[J_{AB} + J_{AC} + J_{AD} + J_{BC} + J_{BD} + J_{CD}]$$

$$a + b + d + g = 0$$

$$c + e + f = 0$$

$$\Delta\bar{\omega} = \tfrac{1}{4}[\Delta\omega_A + \Delta\omega_B + \Delta\omega_C + \Delta\omega_D]$$

$$\Delta\omega_1 = (\Delta\bar{\omega} - \Delta\omega_D); \quad \Delta\omega_2 = (\Delta\bar{\omega} - \Delta\omega_C)$$

$$\Delta\omega_3 = 2\Delta\bar{\omega} - (\Delta\omega_C + \Delta\omega_D); \quad \Delta\omega_4 = (\Delta\bar{\omega} - \Delta\omega_B)$$

$$\Delta\omega_5 = 2\Delta\bar{\omega} - (\Delta\omega_B + \Delta\omega_D); \quad \Delta\omega_6 = 2\Delta\bar{\omega} - (\Delta\omega_B + \Delta\omega_C)$$

$$\Delta\omega_7 = (\Delta\bar{\omega} - \Delta\omega_A)$$

$$\Delta\omega_1 + \Delta\omega_2 + \Delta\omega_4 + \Delta\omega_7 = 0$$

$$\Delta\omega_3 + \Delta\omega_5 + \Delta\omega_6 = 2(\Delta\omega_A - \Delta\bar{\omega})$$

tistical methods, as discussed, for example, by [11]. However, if one or more of the spins are X-spins, the mathematics simplifies considerably. For example, in the *XBCD* system, all the off-diagonal terms $J'_{AB}J'_{AC}$ and J'_{AD} in (21) can be placed equal to zero, and $\mathcal{H}_2$ is reduced, essentially, to four 3 × 3 matrices. Thus analytical solutions in closed form are guaranteed. However, as noted earlier, it is better from the onset, to assume that the projections $(B_z + C_z + D_z)$ and X_z, along the B_0 magnetic field are good quantum numbers, as discussed in the next section.

5. A four spin 1/2 scalar coupled *XBCD* spin system

For ease of comparison with the *ABCD* spin system, we set A equal to X, and write $\mathcal{H}_1$ in the form

$$\mathcal{H}_1 = \hbar[\Delta\bar{\omega}(\mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z) + \Delta\omega_X\mathbf{X}_z] + \bar{J}[\mathbf{B}_z\mathbf{C}_z + \mathbf{B}_z\mathbf{D}_z + \mathbf{C}_z\mathbf{D}_z] + \bar{J}_X(\mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z)\mathbf{X}_z \tag{23}$$

and

$$\begin{aligned}\mathcal{H}_2 = {} & \hbar[(\Delta\omega_A\mathbf{B}_z + \Delta\omega_B\mathbf{C}_z + \Delta\omega_C\mathbf{D}_z) - \Delta\bar{\omega}(\mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z)] \\ & + (J_{BC}\mathbf{B}\cdot\mathbf{C} - \bar{J}\mathbf{B}_z\mathbf{C}_z) + (J_{BD}\mathbf{B}\cdot\mathbf{D} - \bar{J}\mathbf{B}_z\mathbf{D}_z) + (J_{CD}\mathbf{C}\cdot\mathbf{D} - \bar{J}\mathbf{C}_z\mathbf{D}_z) \\ & + (J_{BX} - \bar{J}_x)\mathbf{B}_z\mathbf{X}_z + (J_{CX} - \bar{J}_x)\mathbf{C}_z\mathbf{X}_z + (J_{DX} - \bar{J}_x)\mathbf{D}_z\mathbf{X}_z\,,\end{aligned} \tag{24}$$

where the definitions of $\bar{J}$ and $\bar{J}_x$ can be found in Table 3.

The resultant Hamiltonian for $\mathcal{H}_2$ is block diagonal, and we find

$$[\mathcal{H}_2/\hbar]_{11} = \begin{array}{c|ccccccc|} & 2 & 3 & 5 & 4 & 6 & 7 & 8 \\ \hline 2 & a+\Delta\omega_1 & J'_{CD} & J'_{BD} & & & & \\ 3 & J'_{CD} & b+\Delta\omega_2 & J'_{BC} & & & & \\ 5 & J'_{BD} & J'_{BC} & d+\Delta\omega_4 & & & & \\ 4 & & & & c+\Delta\omega_3 & J'_{BC} & J'_{BD} & \\ 6 & & & & J'_{BC} & e+\Delta\omega_5 & J'_{CD} & \\ 7 & & & & J'_{BD} & J'_{CD} & f+\Delta\omega_6 & \\ 8 & & & & & & & 0 \\ \hline \end{array} \quad (X_z = +\tfrac{1}{2}) \tag{25a}$$

$$[\mathcal{H}_2/\hbar]_{22} = \begin{array}{c|ccccccc|} & 9 & 10 & 11 & 13 & 12 & 14 & 15 \\ \hline 9 & 0 & & & & & & \\ 10 & & f-\Delta\omega_6 & J'_{CD} & J'_{BD} & & & \\ 11 & & J'_{CD} & e-\Delta\omega_5 & J'_{BC} & & & \\ 13 & & J'_{BD} & J'_{BC} & c-\Delta\omega_3 & & & \\ 12 & & & & & d-\Delta\omega_4 & J'_{BC} & J'_{BD} \\ 14 & & & & & J'_{BC} & b-\Delta\omega_2 & J'_{CD} \\ 15 & & & & & J'_{BD} & J'_{CD} & a-\Delta\omega_1 \\ \hline \end{array} \quad (X_z = -\tfrac{1}{2}) \tag{25b}$$

Table 3
Definitions and symmetries for $\mathcal{H}_2$ of eq. (25) for the $XBCD$ spin system.

$a\hbar = \frac{1}{2}(J_{BC} - \bar{J}) - \frac{1}{2}(J_{XD} - \bar{J}_X)$; $\quad b\hbar = \frac{1}{2}(J_{BD} - \bar{J}) - \frac{1}{2}(J_{XC} - \bar{J}_X)$

$c\hbar = \frac{1}{2}(J_{CD} - \bar{J}) + \frac{1}{2}(J_{XB} - \bar{J}_X)$; $\quad d\hbar = \frac{1}{2}(J_{CD} - \bar{J}) - \frac{1}{2}(J_{XB} - \bar{J}_X)$

$e\hbar = \frac{1}{2}(J_{BD} - \bar{J}) + \frac{1}{2}(J_{XC} - \bar{J}_X)$; $\quad f\hbar = \frac{1}{2}(J_{BC} - \bar{J}) + \frac{1}{2}(J_{XD} - \bar{J}_X)$

$\bar{J} = \frac{1}{3}[J_{BC} + J_{BD} + J_{CD}]$; $\quad \bar{J}_X = \frac{1}{3}[J_{XB} + J_{XC} + J_{XD}]$

$a + b + d = 0; c + e + f = 0$

$\Delta\omega_1 = \Delta\bar{\omega} - \Delta\omega_D$; $\quad \Delta\omega_2 = \Delta\bar{\omega} - \Delta\omega_C$

$\Delta\omega_3 = -(\Delta\bar{\omega} - \Delta\omega_B)$; $\quad \Delta\omega_4 = \Delta\bar{\omega} - \Delta\omega_B$

$\Delta\omega_5 = -(\Delta\bar{\omega} - \Delta\omega_C)$; $\quad \Delta\omega_6 = -(\Delta\bar{\omega} - \Delta\omega_D)$

$\Delta\bar{\omega} = \frac{1}{3}[\Delta\omega_B + \Delta\omega_C + \Delta\omega_D]$

$\Delta\omega_1 + \Delta\omega_2 + \Delta\omega_4 = 0$; $\quad \Delta\omega_3 + \Delta\omega_5 + \Delta\omega_6 = 0$

where the coefficients a, b, c, etc., are summarized in Table 3. Note that the Hamiltonian $\mathcal{H}_2$ of (25a, b) is simpler than that of (22) in that (i) two more eigenvalues are identically equal to zero, (ii) the required coefficients have been reduced from $a \approx g$ to $a \approx f$ and $\Delta\omega_1 \approx \Delta\omega_7$ to $\Delta\omega_1 \approx \Delta\omega_6$, (iii) the coefficients $\Delta\omega_1 \approx \Delta\omega_6$ are simpler than those for the $ABCD$ spin system, and (iv) the sum rules of Table 3 are simpler than those of Table 2. It is also worth noting that the quantum states $|8\rangle$ and $|9\rangle$, with eigenvalues zero, correspond to $(A_z + B_z + C_z) = -3/2$ and $(A_z + B_z + C_z) = +3/2$, respectively. Thus the triple quantum operators $\mathbf{A}_-\mathbf{B}_-\mathbf{C}_-$ and $\mathbf{A}_+\mathbf{B}_+\mathbf{C}_+$ for the three ABC spins are constants of the motion under $\mathcal{H}_2$. In essence, therefore, the removal of the spin-flop terms $\mathbf{X}_\pm\mathbf{B}_\mp$, etc., has reduced the problem to that of a BCD spin system.

6. Dipolar coupled spin systems

The method discussed above for scalar coupled spin systems can be easily adapted to deal with the case of dipolar coupled nuclei in the secular approximation. For example, consider the AB spin system, evolving under differing Zeeman offsets and a dipolar interaction. In this case the Hamiltonian takes the form

$$\mathcal{H} = \hbar[(\Delta\omega_A \mathbf{A}_z + \Delta\omega_B \mathbf{B}_z] + D_{AB}[\mathbf{A}_z\mathbf{B}_z - \tfrac{1}{4}(\mathbf{A}^+\mathbf{B}^- + \mathbf{B}^+\mathbf{A}^-)]\,, \tag{26}$$

where (i)

$$D_{AB} = \left\langle \frac{\mu_0 \gamma_A \gamma_B \hbar}{4\pi r_{AB}^3}(1 - 3\cos^2\vartheta_{AB}) \right\rangle, \tag{27}$$

(ii) ϑ_{AB} is the angle made by $\mathbf{r}_{AB}$ with the z-axis, and (iii) the large brackets appearing in (27) imply thermal averaging. Thus we see that in the secular approximation the projection of the angular momentum along the z- axis is conserved. Thus both $(\mathbf{A}_z + \mathbf{B}_z)$ and $\mathbf{A}_z\mathbf{B}_z$ are constants of the motion. Note also that the structure of (26) is very similar to that which applies to the scalar coupled AB spin system, but with minor differences. In the Hamiltonian $\mathcal{H}_1$, the J_{AB} terms are simply replaced by D_{AB}, etc. However, in $\mathcal{H}_2$ the diagonal J_{AB} terms are simply replaced by D_{AB}, etc., while the off-diagonal J_{AB} terms in $\mathcal{H}_2$ must be replaced by replaced by $-(D_{AB}/2)$ etc. Finally, we remark that if necessary it would be possible to deal with mixed scalar and dipole–dipole coupling interactions, simultaneously.

7. A CH_3 dipolar coupled spin system

As an example of the results described in sections 5 and 6, consider an $XBBB$ spin system where the dipolar coupling between the three B spins is identical. Thus

$D_{BC} = D_{BD} = D_{CD} = D$, $D_{BX} = D_{CX} = D_{DX} = D_X$, and $\Delta\omega_B = \Delta\omega_C = \Delta\omega_D = \Delta\omega$. Thus, the Hamiltonian $\mathcal{H}_1$ takes the form

$$\mathcal{H}_1 = \hbar[\Delta\omega(\mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z) + \Delta\omega_X\mathbf{X}_z] + D[\mathbf{B}_z\mathbf{C}_z + \mathbf{B}_z\mathbf{D}_z + \mathbf{C}_z\mathbf{D}_z] + D_X(\mathbf{B}_z + \mathbf{C}_z + \mathbf{D}_z)\mathbf{X}_z\,. \tag{28}$$

Further, using Table 3, it is easily shown that

$$a = b = c = d = f = 0 \tag{29}$$

and

$$\Delta\omega_1 = \Delta\omega_2 = \Delta\omega_3 = \Delta\omega_4 = \Delta\omega_5 = \Delta\omega_6 = 0\,. \tag{30}$$

With these simplifications $(\mathcal{H}_2)_{11}$ takes on the simple form

$$\begin{array}{c} [\mathcal{H}_2/\hbar]_{11} = \\ \\ (X_z = +1/2) \end{array} \quad \begin{array}{c|ccccccc|} & 2 & 3 & 5 & 4 & 6 & 7 & 8 \\ \hline 2 & 0 & D' & D' & & & & \\ 3 & D' & 0 & D' & & & & \\ 5 & D' & D' & 0 & & & & \\ 4 & & & & 0 & D' & D' & \\ 6 & & & & D' & 0 & D' & \\ 7 & & & & D' & D' & 0 & \\ 8 & & & & & & & 0 \\ \hline \end{array} \tag{31}$$

where D' is given by

$$D' = -\tfrac{1}{4}D\,. \tag{32}$$

The eigenvalues of say the top 3×3 matrix given by

$$\lambda_1 = \lambda_2 = -D'; \quad \lambda_3 = 2D' \tag{33}$$

with eigenfunctions

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}[|2\rangle - |5\rangle]\,;$$

$$|\psi_2\rangle = \frac{1}{\sqrt{5}}[|2\rangle - 2|3\rangle + |5\rangle]; \quad |\psi_3\rangle = \frac{1}{\sqrt{3}}[|2\rangle + |3\rangle + |5\rangle]\,, \tag{34}$$

respectively. Note that (i) all the chemical shift information and diagonal dipolar constants are contained in $\mathcal{H}_1$, and (ii) the roots of $\mathcal{H}_2$ are particularly simple, involving only flip-flop terms between the *BBB* spins alone. In this formulation of the problem, it is evident the evolution of the density matrix is primarily dominated by $\mathcal{H}_1$, with small but significant contributions due to $\mathcal{H}_2$.

8. Conclusions

It has been demonstrated that the calculation of the density matrix $\rho(t)$ can be greatly simplified by sub-dividing $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, where $\mathcal{H}_1$ is a suitable linear combination of the constants of the motion. In particular, this technique can be used to obtain closed form solutions for the eigenfunctions and eigenvalues of spin 1/2 *ABC* and *XBCD* spin systems. In particular, it has been shown that the effective size of the $\mathcal{H}_2$ matrix which needs to be considered is reduced from $N \times N$ to at least $(N-2) \times (N-2)$, while for *XBC*... spin systems it is reduced to $(N-4) \times (N-4)$. As a result, the highest rank and highest/lowest order tensor operators are constants of the motion under the action of $\mathcal{H}_2$. Further, by exploiting the fact that $\mathcal{J}_z$ is a good quantum number, it is possible to block-diagonalize the $\mathcal{H}_2$ matrix into no more than 3×3 matrices, for *ABC* and *XBCD* spin systems.

In the following paper, it is shown how the results obtained above can be used to obtain closed form expressions for the time dependence of high-order tensor operators, without recourse to a full diagonalization of the Hamiltonian $\mathcal{H}$.

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