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Analytical block-diagonalization of matrices using unit spherical tensors

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A new method for block-diagonalizing large Hamiltonian matrices, in closed form, is described. The method is based on (i) a general unitary transformation due to Slichter, and (ii) Fano's unit spherical operators $\hat{U}_Q^K(I_i, I_j)$. The method is illustrated with a simple three spin 1/2 dipolar coupled spin system, characterized by off-block-diagonal unit spherical tensors $\hat{U}_0^2(3/2, 1/2, a)$ and $\hat{U}_0^2(3/2, 1/2', a)$. In addition, it is pointed out that any Hamiltonian matrix can be re-labelled in terms of fictitious spin labels, enabling a wide variety of unit spherical tensors to be used in block-diagonalization. For example, a single spin 5/2 matrix can be re-labelled using three spin labels 1/2, 1/2′, and 1/2″, respectively. Thus the tensor algebra required to block-diagonalize a 6×6 matrix is determined solely by the properties of the Pauli spin matrices. Finally, it is shown that re-labelling within the unit spherical tensor framework provides a unifying framework for standard basis operators, fictitious spin 1/2 and 1 operators, and others. The fictitious spin 1/2 unit spherical operators discussed in this paper differ from those of Vega and Pines.

1. Introduction

In the interpretation of NMR experiments on multiple connected spin systems, one is frequently confronted with the need to diagonalize large Hamiltonian matrices. For coupled spin 1/2 nuclei the dimensions of the Hamiltonian are $2^n \times 2^n$, where n is the number of connected spins. Thus for 2(3) spins the size of the Hamiltonian matrix is $4 \times 4 (8 \times 8)$, respectively. If the parameters of the Hamiltonian are known, it is a relatively easy matter to obtain the eigenvalues and eigenvectors using numerical means. However, if the parameters are unknown, it is advantageous to seek solutions in closed form. Given the latter, it is often possible to obtain explicit expressions for the time evolution of the nuclear density matrix $\rho(t)$, a valuable aid in the interpretation of experimental results.

However, in general, there are many cases where solutions in closed form are impossible. Only if the dimensions of the matrix in question are $\leqslant 4 \times 4$, can analytical solutions be guaranteed. Consequently, in the case of more than three coupled spin 1/2 nuclei, solutions in closed form are only possible if the matrix in question can be block-diagonalized into submatrices with dimensions less than 4×4. If this stratagem fails, the only resource is to obtain approximate eigenvalues and eigenvectors using either perturbation theory or Newton's method of successive approximations (see, for example, ref. [1]).

In this paper, the problem of block-diagonalizing large Hamiltonian matrices is addressed within the framework of Fano's unit spherical tensors [2–4]. The basic idea behind this work is that it is easier to block-diagonalize a given matrix than to reduce it to its full diagonal form. As a first step in this direction, a simple three dipolar coupled spin 1/2 problem is examined using geometries other than the simple equilateral triangle considered in ref. [4]. In general, the 8×8 Hamiltonian matrix in question is characterized by the presence of off-block-diagonal unit spherical operators $\hat{U}_0^2(3/2, 1/2, a)$ and $\hat{U}_0^2(3/2, 1/2', a)$, where $I = 3/2, 1/2$, and $1/2'$ are the spin states available to the three spin 1/2 spin system [3,4]. Thus this example provides a simple introduction to the problem of block-diagonalizing large matrices. In particular, it is shown that (i) for the problem in question a perturbative approach used by Slichter [5] can be summed to infinite order, and (ii) this result can be used to "force" block-diagonalization of the 8×8 matrix into two 4×4 matrices. Finally, using the observation that the Zeeman projection $(m_1 + m_2 + m_3)$ is a "good quantum number", the matrix in question is further reduced to a one 2×2 plus two 3×3 matrices. The two distinct methods, which appear to have little in common with each other, are contrasted and discussed in some detail.

For brevity, it will be assumed that the reader is familiar with the terminology and properties of the unit spherical tensors, as discussed in refs. [2–4].

2. Three coupled spin 1/2 problem

Consider the three-spin 1/2 nuclei shown in fig. 1. Here the are vector of the plane formed by the three spins is parallel to the applied magnetic field $\boldsymbol{H}$. However the distances a, b, and c between the spins are not necessarily identical.

Following eq. (24) of ref. [4], the Hamiltonian of the dipolar coupled spin system in the strongly coupled representation can be written as

$$\mathcal{H} = \hbar \Delta\omega \mathcal{J}_z + \alpha \hat{U}_0^2(\tfrac{3}{2}, \tfrac{3}{2}) + \beta \hat{U}_0^2(\tfrac{3}{2}, \tfrac{1}{2}, a) + \gamma \hat{U}_0^2(\tfrac{3}{2}, \tfrac{1}{2}', a) , \tag{1}$$

where (i) the spins available are $I = 3/2, 1/2$, and $1/2'$, respectively, (ii) the unit spherical tensors are defined via

$$\langle I_1 M_1 | \hat{U}_Q^K(I_3, I_4) | I_2 M_2 \rangle = (-1)^{I_2 - M_1} (2K+1)^{1/2} \begin{pmatrix} I_1 & K & I_2 \\ -M_1 & Q & M_2 \end{pmatrix} \delta_{I_1 I_3} \delta_{I_2 I_4} , \tag{2}$$

(iii) the Zeeman offset is given by

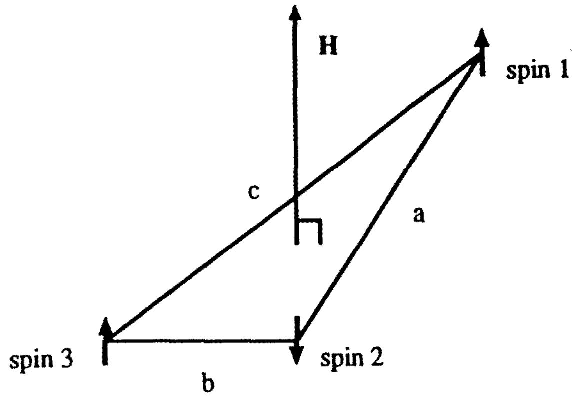

Fig. 1. Three coupled spin 1/2 nuclei. The area vector $\boldsymbol{A}$ of the plane formed by the spins is parallel to $\boldsymbol{H}$. However the distances between the spins a, b, c, are arbitrary

$$\mathcal{H}_z/\hbar = \Delta\omega\mathcal{J}_z = \Delta\omega\left[\sqrt{5}\,\hat{U}_0^1\left(\tfrac{3}{2},\tfrac{3}{2}\right) + \frac{1}{\sqrt{2}}\hat{U}_0^1\left(\tfrac{1}{2},\tfrac{1}{2}\right) + \frac{1}{\sqrt{2}}\hat{U}_0^1\left(\tfrac{1'}{2},\tfrac{1'}{2}\right)\right], \tag{3}$$

in terms of unit tensors, (iv) the coefficients of the dipolar Hamiltonian are

$$\begin{aligned}\alpha &= \frac{1}{2\sqrt{6}}[D_{12} + D_{13} + D_{23}],\\ \beta &= \frac{1}{2\sqrt{3}}[(D_{13} + D_{23}) - 2D_{12}],\\ \gamma &= \tfrac{1}{2}[D_{23} - D_{13}],\end{aligned} \tag{4}$$

and (v)

$$D_{ij} = \frac{\mu_o(g\mu_N)^2}{4\pi r_{ij}^3}\left[1 - 3\,\overline{\cos^2\theta_{ij}}\right]. \tag{5}$$

Here the average over $\cos^2\theta$ implies that the spin system in question may be spinning about some molecular axis, which is not necessarily collinear with the applied field $\boldsymbol{H}$.

Note that the first two terms in eq. (1) are block-diagonal in I, whereas the last two terms are off-block-diagonal. Further, if $D_{12} = D_{13} = D_{23}$, β and γ vanish identically, and the Hamiltonian is block-diagonal in I. This is the case for three identical spins placed at the corners of an equilateral triangle, discussed earlier in ref. [4].

3. Perturbation theory: a unitary transformation

First, we note that the Hamiltonian of eq. (1) can be subdivided into block-diagonal and off-block-diagonal terms:

$$\mathcal{H} = \mathcal{H}_\mathrm{D} + \mathcal{H}_\mathrm{OD}\,, \tag{6}$$

where

$$\mathcal{H}_\mathrm{D} = \hbar\Delta\omega\mathcal{J}_z + \alpha\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2}) \tag{7}$$

and

$$\mathcal{H}_\mathrm{OD} = \beta\hat{U}_0^2(\tfrac{3}{2},\tfrac{1}{2},a) + \gamma\hat{U}_0^2(\tfrac{3}{2},\tfrac{1'}{2},a)\,. \tag{8}$$

Thus we seek a unitary transformation which will reduce $\mathcal{H}$ to the block-diagonal form.

As noted earlier, a similar problem has been tackled by Slichter [5] in connection with the atomic spin–orbit coupling term $\lambda \boldsymbol{l}\cdot\boldsymbol{s}$, which prevents block-diagonalization in the $\boldsymbol{l}$ and $\boldsymbol{s}$ submanifolds. Following ref. [5] therefore, we seek a unitary transformation $\exp(S)$ such that

$$\mathcal{H}' = \mathrm{e}^{-S}\mathcal{H}\mathrm{e}^{+S}\,, \tag{9}$$

where, hopefully, $\mathcal{H}'$ is block-diagonal.

The right-hand side of eq. (9) can be expanded using the nested commutator expansion

$$\mathrm{e}^{-S}\mathcal{H}\mathrm{e}^{+S} = \mathcal{H} - [S,\mathcal{H}]_- + \tfrac{1}{2!}[S,[S,\mathcal{H}]_-]_- - \tfrac{1}{3!}[S,[S,[S,\mathcal{H}]_-]_-] + \dots\,, \tag{10}$$

or alternatively

$$\begin{aligned}\mathrm{e}^{-S}(\mathcal{H}_\mathrm{D} + \mathcal{H}_\mathrm{OD})\mathrm{e}^{+S} = {} & \mathcal{H}_\mathrm{D} + \mathcal{H}_\mathrm{OD} - [S,\mathcal{H}_\mathrm{D}]_- - [S,\mathcal{H}_\mathrm{OD}]_- \\ & + \tfrac{1}{2!}[S,[S,\mathcal{H}_\mathrm{D}]_-]_- + \tfrac{1}{2!}[S,[S,\mathcal{H}_\mathrm{OD}]_-]_- - \dots\,. \end{aligned} \tag{11}$$

If $\mathcal{H}_\mathrm{OD}$ is small, S should be $\approx \mathcal{H}_\mathrm{OD}$, and so the series should converge. Further, if we choose S such that

$$\mathcal{H}_\mathrm{OD} = [S,\mathcal{H}_\mathrm{D}]_-\,, \tag{12}$$

then

$$\begin{aligned}\mathcal{H}' = \mathrm{e}^{-S}(\mathcal{H}_\mathrm{D} + \mathcal{H}_\mathrm{OD})\mathrm{e}^{+S} &= \mathcal{H}_\mathrm{D} - [S,\mathcal{H}_\mathrm{OD}]_- + \tfrac{1}{2!}[S,[S,\mathcal{H}_\mathrm{D}]_-]_- + \mathrm{Ord}(S^3) \\ &= \mathcal{H}_\mathrm{D} - \tfrac{1}{2}[S,\mathcal{H}_\mathrm{OD}]_-\,, \end{aligned} \tag{13}$$

to order S^3. Note that for this strategem to work, S must be off-block-diagonal and such that $[S,\mathcal{H}_\mathrm{OD}]_-$ is block-diagonal.

From the first row of the commutators given in table 1, we see that

$$[\hat{U}_0^2(\tfrac{3}{2},\tfrac{1}{2},s),\, \hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2})]_- = \tfrac{1}{2}\hat{U}_0^2(\tfrac{3}{2},\tfrac{1}{2},a)\,. \tag{14}$$

This suggests therefore that the required operator S is given by

$$S = \frac{2}{\alpha}[\beta\hat{U}_0^2(\tfrac{3}{2},\tfrac{1}{2},s) + \gamma\hat{U}_0^2(\tfrac{3}{2},\tfrac{1'}{2},s)]\,. \tag{15}$$

Moreover, since

Table 1
Some commutators for the three coupled spin 1/2 spin system

$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^2(\frac{3}{2},\frac{3}{2})]_-$	$=\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a)]_-$	$=-\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1}{2})+\frac{1}{2}\hat{U}_0^0(\frac{3}{2},\frac{3}{2})-\frac{1}{\sqrt{2}}\hat{U}_0^0(\frac{1}{2},\frac{1}{2})$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^2(\frac{3}{2},\frac{1'}{2},a)]_-$	$=-\frac{1}{2}\hat{U}_0^2(\frac{1}{2},\frac{1'}{2},s)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^0(\frac{3}{2},\frac{3}{2})]_-$	$=-\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a),\hat{U}_0^0(\frac{3}{2},\frac{3}{2})]_-$	$=-\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^0(\frac{1}{2},\frac{1}{2})]_-$	$=\frac{1}{\sqrt{2}}\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a),\hat{U}_0^0(\frac{1}{2},\frac{1}{2})]_-$	$=\frac{1}{\sqrt{2}}\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},s),\hat{U}_0^0(\frac{1}{2},\frac{1'}{2},s)]_-$	$=\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1'}{2},a)$
$[\hat{U}_0^2(\frac{3}{2},\frac{1}{2},a),\hat{U}_0^0(\frac{1}{2},\frac{1'}{2},s)]_-$	$=\frac{1}{2}\hat{U}_0^2(\frac{3}{2},\frac{1'}{2},s)$

$$[\mathcal{J}_z,\hat{U}_0^2(\tfrac{3}{2},\tfrac{1}{2},s)]=[\mathcal{J}_z,\hat{U}_0^2(\tfrac{3}{2},\tfrac{1'}{2},s)]=0\,, \tag{16}$$

(see for example the Racah-like identities discussed in ref. [1]), the Zeeman term in the Hamiltonian is unaffected by the unitary transformation of eq. (15). In practice, it is usually a simple matter to find S by inspection. However, it is also possible to determine S element by element, using the method set out in appendix D of ref. [5].

With the above choice of S (15), it is easily shown that

$$\begin{aligned}[S,\mathcal{H}_{\mathrm{OD}}]_- = -\Bigg\{&\frac{\beta^2+\gamma^2}{\alpha}[\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2})-\hat{U}_0^0(\tfrac{3}{2},\tfrac{3}{2})]+\frac{\sqrt{2}\beta^2}{\alpha}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1}{2})\\ &+\frac{\sqrt{2}\gamma^2}{\alpha}\hat{U}_0^0(\tfrac{1'}{2},\tfrac{1'}{2})+\frac{2\gamma\beta}{\alpha}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1'}{2},s)\Bigg\}=X\,,\end{aligned} \tag{17}$$

where (i) we have made use of the second and third entries in table 1, and (ii) X is a shorthand notation for this particular commutator. The new transformed Hamiltonian therefore takes the form

$$\begin{aligned}\mathcal{H}' = \mathcal{H}_{\mathrm{D}}-\tfrac{1}{2}[S,\mathcal{H}_{\mathrm{OD}}]_- &= \mathcal{H}_{\mathrm{D}}+\frac{\beta^2+\gamma^2}{2\alpha}[\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2})-\hat{U}_0^0(\tfrac{3}{2},\tfrac{3}{2})]\\ &+\frac{\beta^2}{\alpha\sqrt{2}}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1}{2})+\frac{\gamma^2}{\alpha\sqrt{2}}\hat{U}_0^0(\tfrac{1'}{2},\tfrac{1'}{2})+\frac{\beta\gamma}{\alpha}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1'}{2},s)\end{aligned} \tag{18}$$

to order S^3.

Alternatively, eq. (18) can be re-written in the form

$$\mathcal{H}' = \hbar\Delta\omega\mathcal{J}_z+\alpha'\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2})+\mathcal{H}_{0\mathrm{R}}\,, \tag{19}$$

where (i) the effective strength α' of the second rank dipolar term affecting the spin $I=3/2$ state is now given by

$$\alpha' = \alpha + \frac{\beta^2 + \alpha^2}{2\alpha}\,, \tag{20}$$

and (ii) the zero-rank terms are given by

$$\mathcal{H}_{0\mathrm{R}} = -\frac{\beta^2+\gamma^2}{2\alpha}\hat{U}_0^0(\tfrac{3}{2},\tfrac{3}{2}) + \frac{\beta^2}{\alpha\sqrt{2}}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1}{2})$$
$$+\frac{\gamma^2}{\alpha\sqrt{2}}\hat{U}_0^0(\tfrac{1}{2}',\tfrac{1}{2}') + \frac{\beta\gamma}{\alpha}\hat{U}_0^0(\tfrac{1}{2},\tfrac{1}{2}',s)\,.$$

Thus the 8×8 matrix has been reduced to two 4×4 block-diagonal matrices, to order $\approx S^3$. In summary, therefore, the principal effects of the transformation are (i) to increase the energy separation between the $I = 3/2, 1/2$ and $1/2'$ spin levels through the action of the zero-rank terms, (ii) to modify the strength of the dipolar field term acting on the $I = 3/2$ spin state, and (iii) to cause admixing between the $1/2$ and $1/2'$ spin states. Note that, for convenience, we have used the spin labels $3/2$, $1/2$, $1/2'$ to describe the new partitioned matrices of the 8×8 matrix, even though the original wave functions are now admixed. In summary, therefore, for weak β and γ, NMR experiments should be performed treating the $I = 3/2$ spin system as if it were a single spin system, but with a small change in the dipolar splitting.

Finally, since the manifold spanned by the $I = 3/2$ state is already diagonal, the problem has been reduced to a diagonalization of the 4×4 matrix associated with the $I = 1/2$ and $1/2'$ spin manifolds. After some minor manipulation we find

$$\begin{aligned}
E_1 &= \hbar\Delta\omega + \beta^2/\alpha + 4\beta^2\gamma^2/[\alpha(\beta^2-\gamma^2)]\,,\\
E_2 &= \hbar\Delta\omega + \gamma^2/\alpha + 4\beta^2\gamma^2/[\alpha(\beta^2-\gamma^2)]\,,\\
E_3 &= -\hbar\Delta\omega + \beta^2/\alpha + 4\beta^2\gamma^2/[\alpha(\beta^2-\gamma^2)]\,,\\
E_4 &= -\hbar\Delta\omega + \gamma^2/\alpha + 4\beta^2\gamma^2/[\alpha(\beta^2-\gamma^2)]\,,
\end{aligned} \tag{22}$$

to order S^3 (or $\mathcal{H}_{\mathrm{OD}}^3$).

4. Infinite series: block-diagonalization

Given the success of the perturbative approach described in the previous section, it is natural to enquire whether or not it is possible to do better by going to higher order in S. In fact, it is possible to sum the entire series.

For reasons which will soon become apparent, it is advantageous to modify, slightly, the unitary transformation used in the previous section. In place of eq. (9), therefore, we write

$$\mathcal{H}' = \mathrm{e}^{-\lambda S}\mathcal{H}\mathrm{e}^{+\lambda S}\,, \tag{23}$$

where λ is a constant to be defined later. Next we observe that the left-hand side of eq. (23) is really the sum of two infinite exponential series. Explicitly

$$\begin{aligned}\mathcal{H}' = \mathrm{e}^{-\lambda S}\mathcal{H}\mathrm{e}^{+\lambda S} &= \mathrm{e}^{-\lambda S}\mathcal{H}_{\mathrm{D}}\mathrm{e}^{+\lambda S} + \mathrm{e}^{-\lambda S}\mathcal{H}_{\mathrm{OD}}\mathrm{e}^{+\lambda S} \\ &= +\mathcal{H}_{\mathrm{D}} - \lambda[S,\mathcal{H}_{\mathrm{D}}]_- + \frac{\lambda^2}{2!}[S_2,\mathcal{H}_{\mathrm{D}}]_- \dots \\ &\quad + \mathcal{H}_{\mathrm{OD}} - \lambda[S,\mathcal{H}_{\mathrm{OD}}]_- + \frac{\lambda^2}{2!}[S_2,\mathcal{H}_{\mathrm{OD}}]_- \dots ,\end{aligned} \tag{24}$$

where $[S_2, \mathcal{H}]_-$ is a short-hand notation for $[S, [S, \mathcal{H}]_-]_-$ etc.

The first two single commutators in eq. (24) have already been obtained. On evaluating the double commutator $[S_2, \mathcal{H}_{\mathrm{OD}}]_-$ we find

$$[S_2, \mathcal{H}_{\mathrm{OD}}]_- = -\frac{4(\beta^2+\gamma^2)}{\alpha^2}\mathcal{H}_{\mathrm{OD}} = -\xi^2\mathcal{H}_{\mathrm{OD}} , \tag{25}$$

where (i) we have made use of the commutation relationships summarized in table 1, and (ii) the constant ξ is given by

$$\xi = \frac{2(\beta^2+\gamma^2)^{1/2}}{\alpha} . \tag{26}$$

The appearance of the off-block-diagonal term $\mathcal{H}_{\mathrm{OD}}$ term in eq. (24) means that both the exponential series are "closed" in the sense that only $\mathcal{H}_{\mathrm{OD}}$ and $[S, \mathcal{H}_{\mathrm{OD}}]_-(= X)$ ever appear. Proceeding in this fashion therefore we obtain

$$\begin{aligned}\mathcal{H}' = &+\mathcal{H}_{\mathrm{D}} - \lambda\mathcal{H}_{\mathrm{OD}} + \frac{\lambda^2}{2!}X + \frac{\lambda^3}{3!}\xi^2\mathcal{H}_{\mathrm{OD}} - \frac{\lambda^4}{4!}\xi^2 X \dots \\ &+ \mathcal{H}_{\mathrm{OD}} - \lambda X - \frac{\lambda^2}{2!}\xi^2\mathcal{H}_{\mathrm{OD}} + \frac{\lambda^3}{3!}\xi^2 X + \frac{\lambda^4}{4!}\xi^4\mathcal{H}_{\mathrm{OD}} \dots .\end{aligned} \tag{27}$$

These two series can be summed exactly. We find

$$\mathcal{H}' = \mathcal{H}_{\mathrm{D}} + f\mathcal{H}_{\mathrm{OD}} + g[S, \mathcal{H}_{\mathrm{OD}}]_- , \tag{28}$$

where

$$f = \left[\cos\lambda\xi - \frac{1}{\xi}\sin\lambda\xi\right] \tag{29}$$

and

$$g = \left[\frac{1-\cos\lambda\xi}{\xi^2} - \frac{\sin\lambda\xi}{\xi}\right] . \tag{30}$$

We are now in a position to make an interesting observation. If we choose λ such that

$$\tan\lambda\xi = \xi , \tag{31}$$

the coefficient f associated with the off-block-diagonal Hamiltonian $\mathcal{H}_{\mathrm{OD}}$ vanishes identically. Further, given eq. (30) it is easy to show that the coefficient g is now of the form

$$g = -\frac{\alpha}{\alpha + \eta}, \tag{32}$$

where η is given by

$$\eta = [\alpha^2 + 4(\beta^2 + \gamma^2)]^{1/2}. \tag{33}$$

Thus the Hamiltonian takes the form

$$\begin{aligned}\mathcal{H}' &= \mathcal{H}_{\mathrm{D}} + g(\lambda)[S, \mathcal{H}_{\mathrm{OD}}]_- = \hbar\Delta\omega\mathcal{J}_z + \alpha\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2}) \\ &+ \frac{1}{\alpha+\eta}\{(\beta^2+\gamma^2)[\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2}) - \hat{U}_0^0(\tfrac{3}{2},\tfrac{3}{2})] \\ &+ \sqrt{2}\beta^2\hat{U}_0^0(\tfrac{1}{2},\tfrac{1}{2}) + \sqrt{2}\gamma^2\hat{U}_0^0(\tfrac{1'}{2},\tfrac{1'}{2}) + 2\beta\gamma\hat{U}_0^0(\tfrac{1}{2},\tfrac{1'}{2},s)\Big\},\end{aligned} \tag{34}$$

which spans the block-diagonal 4×4 submanifold of the $I = 3/2$ state, and the 4×4 submanifold of the $I = 1/2$ and $1/2'$ states.

In summary, therefore, a procedure for block-diagonalizing an 8×8 matrix has been described, within the framework of unit spherical operators. In the next section, an alternative method is presented which allows the same matrix to be block- diagonalized into one 2×2 and two 3×3 matrices.

5. Block-diagonalization using $\mathcal{J}_z$ as a good quantum number

So far we have not *fully* exploited the fact that $\mathcal{J}_z$ commutes with the Hamiltonian of eq. (1). Since the projection of $\mathcal{J}_z$ along the z-axis is a "good quantum number", it is advantageous to re-label the Hamiltonian matrix in terms of $|M_z = 3/2\rangle, |M_z = 1/2\rangle$, etc. Proceeding in this fashion, we obtain the Hamiltonian matrix

$$\mathcal{H} = \tfrac{1}{2} \times \begin{array}{c} \begin{array}{cccccccc} |\tfrac{3}{2}\,\tfrac{3}{2}\rangle & |\tfrac{3}{2} - \tfrac{3}{2}\rangle & |\tfrac{3}{2}\,\tfrac{1}{2}\rangle & |\tfrac{1}{2}\,\tfrac{1}{2}\rangle & |\tfrac{1'}{2} - \tfrac{1}{2}\rangle & |\tfrac{3}{2} - \tfrac{1}{2}\rangle & |\tfrac{1}{2} - \tfrac{1}{2}\rangle & |\tfrac{1'}{2} - \tfrac{1}{2}\rangle \end{array} \\ \begin{pmatrix} \alpha + 3\hbar\Delta\omega & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha - 3\hbar\Delta\omega & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar\Delta\omega - \alpha & -\beta & -\gamma & 0 & 0 & 0 \\ 0 & 0 & -\beta & \hbar\Delta\omega & 0 & 0 & 0 & 0 \\ 0 & 0 & -\gamma & 0 & \hbar\Delta\omega & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\alpha - \hbar\Delta\omega & \beta & \gamma \\ 0 & 0 & 0 & 0 & 0 & \beta & -\hbar\Delta\omega & 0 \\ 0 & 0 & 0 & 0 & 0 & \gamma & 0 & -\hbar\Delta\omega \end{pmatrix} \end{array} \tag{35}$$

which consists of one 2×2 matrix and two 3×3 block-diagonal matrices. These small matrices are easily diagonalized to yield the eigenvalues and eigenvectors summarized in table 2.

From an examination of table 2, it is clear that from a multiple-quantum point of view, the triple quantum frequency of $3\Delta\omega$ is unaffected by the presence of the

Table 2
The eigenvalues and eigenvectors of the Hamiltonian of eq. (1), in the strongly coupled representation.

$E_1 = \frac{1}{2}(\alpha + 3\hbar\Delta\omega)$	$\|\psi_1\rangle = \|\frac{3}{2},\frac{3}{2}\rangle$
$E_2 = \frac{1}{2}(\alpha - 3\hbar\Delta\omega)$	$\|\psi_2\rangle = \|\frac{3}{2},-\frac{3}{2}\rangle$
$E_3 = \frac{1}{2}\hbar\Delta\omega$	$\|\psi_3\rangle = \frac{1}{\sqrt{\beta^+\gamma^2}}(\gamma\|\frac{1}{2},\frac{1}{2}\rangle - \beta\|\frac{1}{2}',\frac{1}{2}\rangle)$
$E_4 = \frac{1}{2}(\hbar\Delta\omega + \frac{1}{2}(\eta - \alpha))$	$\|\psi_4\rangle = \frac{1}{\sqrt{2\eta(\eta-\alpha)}}((\eta-\alpha)\|\frac{3}{2},\frac{1}{2}\rangle - 2\beta\|\frac{1}{2},\frac{1}{2}\rangle - 2\gamma\|\frac{1}{2}',\frac{1}{2}\rangle)$
$E_5 = \frac{1}{2}(\hbar\Delta\omega - \frac{1}{2}(\eta + \alpha))$	$\psi_5\rangle = \frac{1}{\sqrt{2\eta(\eta+\alpha)}}((\eta+\alpha)\|\frac{3}{2},\frac{1}{2}\rangle + 2\beta\|\frac{1}{2},\frac{1}{2}\rangle + 2\gamma\|\frac{1}{2}',\frac{1}{2}\rangle)$
$E_6 = -\frac{1}{2}\hbar\Delta\omega$	$\|\psi_6\rangle = \frac{1}{\sqrt{\beta^+\gamma^2}}(\gamma\|\frac{1}{2},-\frac{1}{2}\rangle - \beta\|\frac{1}{2}',-\frac{1}{2}\rangle)$
$E_7 = \frac{1}{2}(-\hbar\Delta\omega + \frac{1}{2}(\eta - \alpha))$	$\|\psi_7\rangle = \frac{1}{\sqrt{2\eta(\eta-\alpha)}}(\eta-\alpha)\|\frac{3}{2},-\frac{1}{2}\rangle + 2\beta\|\frac{1}{2},-\frac{1}{2}\rangle + 2\gamma\|\frac{1}{2}',-\frac{1}{2}\rangle)$
$E_8 = \frac{1}{2}(-\hbar\Delta\omega - \frac{1}{2}(\eta + \alpha))$	$\|\psi_8\rangle = \frac{1}{\sqrt{2\eta(\eta+\alpha)}}(\eta+\alpha)\|\frac{3}{2},-\frac{1}{2}\rangle - 2\beta\|\frac{1}{2},-\frac{1}{2}\rangle - 2\gamma\|\frac{1}{2}',-\frac{1}{2}\rangle)$
where $\eta = \sqrt{\alpha^2 + 4(\beta^2+\gamma^2)}$	

off-diagonal terms β and γ. However, this is not the case for most of the single and double quantum frequencies, unless of course β and γ are identically equal to zero.

Using table 2, it is easily shown that the characteristic equation of the Hamiltonian is of the form

$$|\mathcal{H} - \lambda I| = \left[\left(\lambda - \frac{3\hbar\Delta\omega}{2} - \frac{\alpha}{2}\right)\left(\lambda + \frac{3\hbar\Delta\omega}{2} - \frac{\alpha}{2}\right)\left(\lambda - \frac{\hbar\Delta\omega}{2} + \tfrac{1}{4}(\alpha+\eta)\right)\right.$$
$$\left.\times\left(\lambda + \frac{\hbar\Delta\omega}{2} + \tfrac{1}{4}(\alpha+\eta)\right)\right] \times \left[\left(\lambda - \frac{\hbar\Delta\omega}{2}\right)\left(\lambda + \frac{\hbar\Delta\omega}{2}\right)\right.$$
$$\left.\times\left(\lambda - \frac{\hbar\Delta\omega}{2} - \tfrac{1}{4}(\eta-\alpha)\right)\left(\lambda + \frac{\hbar\Delta\omega}{2} - \tfrac{1}{4}(\eta-\alpha)\right)\right]. \qquad (36)$$

The first term in square brackets is associated with the pseudo spin 3/2 submanifold, and the second term by the pseudo spin 1/2 and 1/2′ (4 × 4) submatrix. This statement is easily verified by working out the characteristic equation of the transformed Hamiltonian of eq. (34). For example, for the pseudo spin 3/2 submanifold of the matrix, we have

$$\mathcal{H}(\tfrac{3}{2},\tfrac{3}{2}) = \hbar\Delta\omega I_z(\tfrac{3}{2}) + \alpha\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2}) + \frac{\eta-\alpha}{4}[\hat{U}_0^2(\tfrac{3}{2},\tfrac{3}{2}) - \hat{U}_0^0(\tfrac{3}{2},\tfrac{3}{2})], \qquad (37)$$

or in matrix form

$$\mathcal{H}(\tfrac{3}{2},\tfrac{3}{2}) = \begin{pmatrix} \frac{3}{2}\hbar\Delta\omega + \dfrac{\alpha}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2}\hbar\Delta\omega - \dfrac{\eta+\alpha}{4} & 0 & 0 \\ 0 & 0 & -\frac{1}{2}\hbar\Delta\omega - \left(\dfrac{\eta+\alpha}{4}\right) & 0 \\ 0 & 0 & 0 & -\frac{3}{2}\hbar\Delta\omega + \dfrac{\alpha}{2} \end{pmatrix}, \quad (38)$$

in accord with the first square bracket of the characteristic equation (36).

One final point should be made before concluding this section. From an examination of the eigenvalues of eq. (36), it is evident that it is not possible to distinguish between the coefficients β and γ. They always appear in the combination $\beta^2 + \gamma^2$.

6. Summation of infinite series: a general method

It should, of course, be acknowledged that the three spin problem discussed in this paper is relatively simple in that the Hamiltonian matrix can be block-diagonalized, simple, without recourse to unit spherical tensors. Nevertheless, the results obtained demonstrate the viability of the unit spherical tensor approach. In more complicated problems, it may prove difficult to sum the nested commutator expansion. Thus it is advantageous to seek a more general approach.

Firstly, we assume that a transformation S can be found such that

$$[S, \mathcal{H}_{\mathrm{D}}]_- = \mathcal{H}_{\mathrm{OD}}, \quad (39)$$

where the diagonal and off-diagonal Hamiltonians $\mathcal{H}_{\mathrm{D}}$ and $\mathcal{H}_{\mathrm{OD}}$ are now general. Thus we seek to evaluate the expression

$$\mathcal{H}' = \mathrm{e}^{-\lambda S}\mathcal{H}\mathrm{e}^{+\lambda S}. \quad (40)$$

Secondly, since the unit spherical tensors form a complete set, any Hamiltonian can be expressed in form

$$\mathcal{H}' = \sum_{I_i,I_j}\sum_{K,Q}\sum_{\epsilon} \rho_Q^K(I_i,I_j,\epsilon)\,\hat{U}_Q^K(I_i,I_j,\epsilon), \quad (41)$$

where the Fano coefficients are given by

$$\rho_Q^K(I_i,I_j,\epsilon) = \mathrm{Tr}[(\hat{U}_Q^K(I_i,I_j,\epsilon))^{\dagger}\mathrm{e}^{-\lambda S}\mathcal{H}\mathrm{e}^{+\lambda S}]. \quad (42)$$

Consequently, if the eigenvalues E_N and eigenfunctions $|S_N\rangle$ of S are known, the required Fano coefficients can be rewritten in the form

$$\rho_Q^K(I_i,I_j,\epsilon) = \sum_{N,M} \langle S_N|(\hat{U}_Q^K(I_i,I_j,\epsilon))^{\dagger}|S_M\rangle\langle S_M|\mathcal{H}|S_N\rangle \mathrm{e}^{-\lambda(E_M-E_n)}. \quad (43)$$

Thus the problem of diagonalizing the Hamiltonian $\mathcal{H}$ has been reduced to the problem of diagonalizing S, which is a far simpler problem. For the three spin 1/2 problem considered in this paper, the unitary transformation is given by

$$S = \frac{1}{\alpha} \times \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\beta & 0 & -\gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & 0 & \gamma \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & \gamma & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\gamma & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{44}$$

which, after re-labelling, is readily diagonalized. The eigenvalues consist of six roots with eigenvalue zero, two repeated roots with eigenvalue $+\mathrm{i}\sqrt{\gamma^2+\beta^2}$, and two repeated roots with eigenvalue $-\mathrm{i}\sqrt{\gamma^2+\beta^2}$. This observation strengthens our initial supposition that it is easier to block-diagonalize a given matrix than to reduce it to its energy representation. Proceeding in this fashion, therefore, it is possible to determine all of the Fano coefficients which determine the transformed Hamiltonian $\mathcal{H}'$. Finally, $\mathcal{H}'$ can be reduced to a block-diagonal form with an appropriate selection of the adjustable parameter λ.

7. Fictitious spin labels

So far, the problem of three coupled spin 1/2 nuclei has been addressed in terms of the three angular momenta 3/2, 1/2, 1/2′ available to the nuclear spin system in question. However, it is worth noting that the 8×8 Hamiltonian matrix could equally well have been re-labelled, from the start, in terms of two "fictitious spins" 3/2 and 3/2′ $(4+4=8)$, or two "fictitious spins" 2 and 1 $(5+3=8)$. In fact any Hamiltonian matrix can be re-labelled using a suitable set of "fictitious spins". For example, the 6×6 Hilbert space of a "real" single spin $I = 5/2$ could be re-labelled in terms of two "fictitious" spins $I_1 = 3/2$ and $I_2 = 1/2$. Some possible spin labels for matrices with dimensions less than 10×10 can be seen in table 3. Clearly, each problem should be addressed on its own merits. Note that it is not possible to mix integer and half-integer spins using unit spherical tensors of integer rank $(K = 0, 1, 2, \ldots)$, by virtue of the triangular vector-coupling rule.

Three other points should also be made. In the first place, any matric dimension n can be re-labelled with spins $(0_1, 0_2, 0_3, \ldots, 0_n)$ where the individual spins 0_i are different. In practice, this corresponds to the standard basis set, since all entries in the 1×1 manifold spanned by the submanifold $0_i \times 0_j$ are either 0 or 1 (see, for example, ref. [6] or [7]). Thus the re-labelling scheme proposed in this paper has, as its trivial limit, the standard basis set. Secondly, we note that all half-integer spin systems can be re-labelled with spins $(1/2, 1/2', 1/2'', \ldots, 1/2^n)$. Thus the tensor algebra is reduced to that of the 2×2 Pauli matrices, which can only support rank 0 or 1 tensors. However, while these fictitious spin 1/2 unit spherical operators bear some resemblance to the "fictitious spin 1/2 operators" of Vega and Pines [8], and the "single transition operators" of Wokaun and Ernst [9], they are not identical. For example it is not possible to use unit spherical fictitious spin 1/2 operators for $I = 1$ spin systems. In fact unit spherical spin 1/2 operators cannot be used for integer spin systems. In such cases, it is necessary to use either fictitious spin 1 or 0 operators, as shown in table 3.

8. Conclusions

In this paper, a systematic method for block-diagonalizing Hamiltonian matrices in a closed form has been described, using a simple three spin 1/2 dipolar-coupled nuclei as an example. In particular, it has been shown that unit spherical tensors can be used to block-diagonalize an 8×8 matrix into two 4×4 matrices by (i) summing an infinite series, and (ii) suitably choosing an adjustable parameter. In addition, a simpler method of block-diagonalizing the matrix in question has been described, which made full use of the symmetry in the problem (i.e. $[\mathcal{J}_z, \mathcal{H}]_- = 0$). Both approaches lead, of course, to the same set of eigenvalues. In summary, therefore, one should strive to exploit all of the symmetries resident in the Hamiltonian to the full, particularly for large spin-systems. However, once this has been done, the only hope for further block-diagonalization presumably rests

Table 3
Some fictitious spin labels for matrices with dimensions $\leqslant 10$. Not all possibilities are listed.

Dimensions	Spin labels
1	0
2	$\frac{1}{2}, 0+0'$
3	$1, 0+0'+0''$
4	$\frac{3}{2}, \frac{1}{2}+\frac{1}{2}', 1+0$
5	$2, 1+0+0'$
6	$\frac{5}{2}, \frac{3}{2}+\frac{1}{2}, \frac{1}{2}+\frac{1}{2}'+\frac{1}{2}'', 1+1'$
7	$3, 1+1'+0$
8	$\frac{7}{2}, \frac{5}{2}+\frac{1}{2}, \frac{3}{2}+\frac{3}{2}', 2+1, 1+1'+0+0'$
9	$4, 2+1+0, 3+0+0'$
10	$\frac{9}{2}, \frac{7}{2}+\frac{1}{2}, \frac{5}{2}+\frac{3}{2}, \frac{5}{2}+\frac{1}{2}+\frac{1}{2}', \frac{3}{2}+\frac{3}{2}'+\frac{1}{2}$

with the spherical tensor method described in this paper. However should this stratagem fail, it is still possible to develop a high order block-diagonal perturbation series, in a systematic fashion.

In addition, it has been demonstrated that any matrix can be partitioned using a wide variety of fictitious spin labels. Unit spherical tensors provide an underlying framework for standard basis operators, fictitious spin 1/2, unit spherical operators and others. For example, a single spin 5/2 (6×6) matrix can be re-labelled using spins 1/2, 1/2′, and 1/2″, respectively. Thus the block-diagonalization of the (6×6) matrix is determined by the algebra of the Pauli spin matrices.

Finally, it has been pointed out that it is not possible to partition a given matrix into mixtures of integer and half-integer spins, using unit spherical tensors $\hat{U}_Q^K(I_i, I_j)$ of integer rank K. In a following paper, however, it will be demonstrated that this impasse can be overcome by defining a new set of half-integer rank unit spherical tensors.

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