Complete solution for two coupled spin-1/2 nuclei evolving under chemical shift and dipolar interaction

G.J. Bowden and M.J. Prandolini

School of Physics, University of New South Wales, Sydney, NSW 2052, Australia

Received 16 September 1993; revised 21 March 1994

The spin dynamics for two coupled spin-1/2 nuclei evolving under isotropic chemical shifts and a dipole–dipole interaction, in the high-field limit, is presented using Fano's unit spherical tensors $\hat{U}_Q^K(I_i, I_j)$ as a basis set. For simplicity, relaxation effects are ignored. The results are used to discuss the frequently used dipole–dipole approximations for both homonuclear and heteronuclear spin systems. In particular, it is shown that it is possible to analyse NMR spectra of two spin-1/2 systems where the chemical shift differences and the dipolar interactions are of similar magnitude.

1. Introduction

In an earlier paper [1], it was demonstrated that Fano's unit spherical operators $\hat{U}_Q^K(I_1, I_2)$ can be used to simplify the algebra required to describe the spin dynamics of two spin-1/2 nuclei, evolving under the combined action of scalar coupling and Zeeman offset. For example, from a comparison of unit spherical tensor operators $\hat{U}_Q^K(I_1, I_2)$ with coupled irreducible operators $\hat{T}_Q^K(k_1, k_2)$ [2], it was shown that the use of the former could be used to reduce the number of terms in the density matrix required for a complete solution of AA spin systems by up to 50%. This has clear implications for three or more coupled spin systems. In particular, it should be noted that regardless of the number of spins involved only one Clebsch–Gordan coefficient is required for unit spherical operators. This is in marked contrast to the coupled irreducible tensor operators $\hat{T}_Q^K(k_1, \ldots k_n)$, where it is necessary to evaluate concatenated Clebsch–Gordan coefficients, repeatedly.

To our knowledge no one has given the full solution for two coupled spin system evolving under the combined action of a magnetic dipole–dipole interaction and differing resonant offsets, at least in terms of unit spherical operators. Since the dipole–dipole interaction often plays an important role in determination of (i) structures, (ii) order in aligned molecules, and (iii) multiple quantum transitions, the neatest solution of this problem should be of interest. In this paper, the com-

plete solution, for both homonuclear AA, AB and heteronuclear AX spin systems is presented and discussed, in the secular approximation.

The definition of a unit spherical operator is given by

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

where I_1 and I_2 represent the coupled spin manifolds. To reflect the Hermitian nature of the Hamiltonian and the density matrix, it is advantageous to define the symmetric and antisymmetric combinations

$$\hat{U}^K_Q(I_1,I_2,s) = \frac{1}{\sqrt{2}}(\hat{U}^K_Q(I_1,I_2) + \hat{U}^K_{-Q}(I_2,I_1))\,,$$

$$\hat{U}^K_Q(I_1,I_2,a) = \frac{1}{\sqrt{2}}(\hat{U}^K_Q(I_1,I_2) - \hat{U}^K_{-Q}(I_2,I_1))\,. \tag{2}$$

Note that the $1/\sqrt{2}$ ensures that orthonormality of the symmetric and antisymmetric combination is preserved, i.e.

$$\mathrm{Tr}\left[(\hat{U}^K_Q(I_1,I_2,\alpha))^\dagger \hat{U}^{K'}_{Q'}(I_3,I_4,\alpha')\right] = \delta_{I_1 I_3}\delta_{I_2 I_4}\delta_{\alpha\alpha'}\delta_{KK'}\delta_{QQ'}\,. \tag{3}$$

2. Two coupled spins evolving under dipolar and chemical shift interaction

In the decoupled representation the Hamiltonian for two coupled spins evolving under a Zeeman offset and a dipolar interaction, can be written in the form

$$\mathcal{H} = \hbar(\Delta\omega_1 I_{1z} + \Delta\omega_2 I_{2z}) + D(I_{1z}I_{2z} - \tfrac{1}{4}(I_1^+ I_2^- + I_1^- I_2^+))\,, \tag{4}$$

where (i) we have effected a transformation to the rotating frame, (ii)

$$D = \frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi}\left\langle\frac{1-3\cos^2\theta_{12}}{r_{12}^3}\right\rangle, \tag{5}$$

(iii) $\Delta\omega_{1,2}$ are the resonant offsets for the spins, (iv) r_{12} is the vector joining the two spins and (v) θ_{12} is the angle made by r_{12} with the z-axis.

In the coupled representation, two spin-1/2 nuclei couple to form either $I = 1$ or 0. On transforming eq. (4) into unit spherical tensors, where I_1 and I_2 take on values (1 or 0), we find

$$\mathcal{H} = \hbar(\sqrt{2}\Delta\bar{\omega}\hat{U}^1_0(1,1) + \sqrt{2}\delta\hat{U}^1_0(0,1,a)) + \frac{\sqrt{6}}{4}D\hat{U}^2_0(1,1)\,, \tag{6}$$

where

$$\Delta\bar{\omega} = \tfrac{1}{2}(\Delta\omega_1 + \Delta\omega_2), \quad \delta = \tfrac{1}{2}(\Delta\omega_1 - \Delta\omega_2)\,. \tag{7}$$

Since $\hat{U}_0^1(0,1,a)$ does not commute with $\hat{U}_0^2(1,1)$, it is not possible to separate the Zeeman $\mathcal{H}_Z$ and the dipolar terms $\mathcal{H}_D$ in the evolution operator $\mathcal{U}(t) = e^{-i(\mathcal{H}_Z+\mathcal{H}_D)t/\hbar}$, unless δ is identically equal to zero.

The time evolution for all tensors $\hat{U}_Q^K(I_1, I_2, \alpha)$ ($\alpha = s, a, K \leqslant 2$), evolving under the Hamiltonian (6), is given in table 1. Note that the antisymmetric and symmetric form of the tensors $\hat{U}_0^1(1,0,s)$ and $\hat{U}_0^1(0,1,a)$, respectively, are not given because both $(\hat{U}_0^1(1,0,s), \hat{U}_0^1(0,1,s))$ and $(\hat{U}_0^1(0,1,a), \hat{U}_0^1(1,0,a))$ are linear combinations of each other. This table was prepared using *Mathematica*[1] to project out the necessary time dependent coefficients. For example, the coefficients of the unit spherical tensors are given by

$$\rho_Q^K(I_1, I_2, \alpha, t) = \mathrm{Tr}\left[\hat{U}_Q^K(I_1, I_2, \alpha)^\dagger e^{-i\mathcal{H}t/\hbar}\rho(0)e^{i\mathcal{H}t/\hbar}\right], \tag{8}$$

where $\rho(0)$ is the density matrix at $t = 0$. The evolution of the unit spherical tensors under "hard" rf-pulses, along the x and y axes for two coupled spin, has already been given in tables 10(a) and (b) of [1].

3. Common approximations for dipolar coupled spins

The Hamiltonian of eq. (4) is the high-field approximation for two dipolar coupled spins [3]. However, in the literature two further approximations are frequently employed to simplify the calculations.

For two unlike spins, the flip-flop term $I_1^+ I_2^- + I_1^- I_2^+$ is usually dropped because this term involves an exchange of energy. Within this approximation

$$\mathcal{H}_{ul} = \hbar(\Delta\omega_1 I_{1z} + \Delta\omega_2 I_{2z}) + D I_{1z} I_{2z}, \tag{9}$$

and we see that, unlike in eq. (4), the chemical shift and dipolar terms now commute. This simple approximation greatly simplifies the evolution tables because evolution under the chemical shift and effective dipole–dipole interaction can now be separated [3].

For two nearly alike spins, eq. (4) is often written in the form

$$\mathcal{H} = \hbar(\Delta\omega_1 I_{1z} + \Delta\omega_2 I_{2z}) + D(\tfrac{3}{2} I_{1z} I_{2z} - \tfrac{1}{2}\mathbf{I}_1 \cdot \mathbf{I}_2), \tag{10}$$

and it is customary to drop the scalar term $\mathbf{I}_1 \cdot \mathbf{I}_2$ [4]. This results in the Hamiltonian

$$\mathcal{H}_l = \hbar(\Delta\omega_1 I_{1z} + \Delta\omega_2 I_{2z}) + \tfrac{3}{2} D I_{1z}, I_{2z}, \tag{11}$$

and we see that the form of $\mathcal{H}_l$ is the same as that for $\mathcal{H}_{ul}$ for unlike spins except that the strength of the dipole–dipole coupling is 3/2 times stronger. Once again the evolution tables are deceptively simple because the chemical shift and dipolar terms appearing in eq. (11) commute.

[1] *Mathematica* is a registered trademark of Wolfram Research, Inc.

Table 1
Evolution of the unit spherical tensors $\hat{U}_Q^K(I_i, I_j, \alpha), \alpha = s, a$, under the influence of a chemical shift and dipolar coupling. For the evolution of the antisymmetric tensors (not explicitly included), replace a by s and s by a. This table holds for both AB and AX systems.

$$\mathcal{U}\hat{U}_0^0(0,0)\mathcal{U}^\dagger = \hat{U}_0^0(0,0)(D^2 + 8\delta^2(1+\cos\lambda_{12}t))/R^2 + \hat{U}_0^0(1,1)8\delta^2(1-\cos\lambda_{12}t)/(\sqrt{3}R^2)$$
$$- i\hat{U}_0^1(1,0,s)2\sqrt{2}\delta(\sin\lambda_{12}t)/R + \hat{U}_0^1(0,1,a)2\sqrt{2}D\delta(1-\cos\lambda_{12}t)/R^2$$
$$- \hat{U}_0^2(1,1)16\delta^2(1-\cos\lambda_{12}t)/(\sqrt{6}R^2)$$

$$\mathcal{U}\hat{U}_0^0(1,1)\mathcal{U}^\dagger = \hat{U}_0^0(0,0)8\delta^2(1-\cos\lambda_{12}t)/(\sqrt{3}R^2) + \hat{U}_0^0(1,1)(5R^2 + D^2 + 16\delta^2\cos\lambda_{12}t)/(6R^2)$$
$$+ i\hat{U}_0^1(1,0,s)4\delta(\sin\lambda_{12}t)/(\sqrt{6}R) - \hat{U}_0^1(0,1,a)4D\delta(1-\cos\lambda_{12}t)/(\sqrt{6}R^2)$$
$$+ \hat{U}_0^2(1,1)\sqrt{2}(R^2 - D^2 - 16\delta^2\cos\lambda_{12}t)/(6R^2)$$

$$\mathcal{U}\hat{U}_0^1(1,0,s)\mathcal{U}^\dagger = -i\hat{U}_0^0(0,0)2\sqrt{2}\delta(\sin\lambda_{12}t)/R + i\hat{U}_0^0(1,1)2\sqrt{6}\delta(\sin\lambda_{12}t)/(3R)$$
$$+ \hat{U}_0^1(1,0,s)\cos\lambda_{12}t + i\hat{U}_0^1(0,1,a)D(\sin\lambda_{12}t)/R$$
$$- i\hat{U}_0^2(1,1)4\delta(\sin\lambda_{12}t)/(\sqrt{3}R^2)$$

$$\mathcal{U}\hat{U}_1^1(1,0,s)\mathcal{U}^\dagger = \hat{U}_1^1(1,0,s)(A\cos\lambda_{14}t + B\cos\lambda_{24}t)/R + i\hat{U}_1^1(1,0,a)(A\sin\lambda_{14}t + B\sin\lambda_{24}t)/R$$
$$- i\hat{U}_1^1(1,1,s)\sqrt{2}\delta(\sin\lambda_{14}t - \sin\lambda_{24}t)/R - \hat{U}_1^1(1,1,a)\sqrt{2}\delta(\cos\lambda_{14}t - \cos\lambda_{24}t)/R$$
$$- i\hat{U}_1^2(1,1,s)\sqrt{2}\delta(\sin\lambda_{14}t - \sin\lambda_{24}t)/R - \hat{U}_1^2(1,1,a)\sqrt{2}\delta(\cos\lambda_{14}t - \cos\lambda_{24}t)/R$$

$$\mathcal{U}\hat{U}_0^1(0,1,a)\mathcal{U}^\dagger = \hat{U}_0^0(0,0)2\sqrt{2}D\delta(1-\cos\lambda_{12}t)/R^2 - \hat{U}_0^0(1,1)2\sqrt{6}D\delta(1-\cos\lambda_{12}t)/(3R^2)$$
$$+ i\hat{U}_0^1(1,0,s)D(\sin\lambda_{12}t)/R + \hat{U}_0^1(0,1,a)(16\delta^2 + D^2\cos\lambda_{12}t)/R^2$$
$$+ \hat{U}_0^2(1,1)4D\delta(1-\cos\lambda_{12}t)/(\sqrt{3}R^2)$$

$$\mathcal{U}\hat{U}_1^1(0,1,s)\mathcal{U}^\dagger = \hat{U}_1^1(0,1,s)(A\cos\lambda_{13}t + B\cos\lambda_{23}t)/R - i\hat{U}_1^1(0,1,a)(A\sin\lambda_{13}t + B\sin\lambda_{23}t)/R$$
$$+ i\hat{U}_1^1(1,1,s)\sqrt{2}\delta(\sin\lambda_{13}t - \sin\lambda_{23}t)/R - \hat{U}_1^1(1,1,a)\sqrt{2}\delta(\cos\lambda_{13}t - \cos\lambda_{23}t)/R$$
$$- i\hat{U}_1^2(1,1,s)\sqrt{2}\delta(\sin\lambda_{13}t - \sin\lambda_{23}t)/R + \hat{U}_1^2(1,1,a)\sqrt{2}\delta(\cos\lambda_{13}t - \cos\lambda_{23}t)/R$$

$$\mathcal{U}\hat{U}_0^1(1,1)\mathcal{U}^\dagger = \hat{U}_0^1(1,1) - \text{ a constant of the motion}$$

$$\mathcal{U}\hat{U}_1^1(1,1,s)\mathcal{U}^\dagger = -i\hat{U}_1^1(1,0,s)\sqrt{2}\delta(\sin\lambda_{14}t - \sin\lambda_{24}t)/R - \hat{U}_1^1(1,0,a)\sqrt{2}\delta(\cos\lambda_{14}t - \cos\lambda_{24}t)/R$$
$$+ i\hat{U}_1^1(0,1,s)\sqrt{2}\delta(\sin\lambda_{13}t - \sin\lambda_{23}t)/R - \hat{U}_1^1(0,1,a)\sqrt{2}\delta(\cos\lambda_{13}t - \cos\lambda_{23}t)/R$$
$$+ \hat{U}_1^1(1,1,s)(B(\cos\lambda_{13}t + \cos\lambda_{14}t) + A(\cos\lambda_{23}t + \cos\lambda_{24}t))/(2R)$$
$$- i\hat{U}_1^1(1,1,a)(B(\sin\lambda_{13}t - \sin\lambda_{14}t) + A(\sin\lambda_{23}t - \sin\lambda_{24}t))/(2R)$$
$$- \hat{U}_1^2(1,1,s)(B(\cos\lambda_{13}t - \cos\lambda_{14}t) + A(\cos\lambda_{23}t - \cos\lambda_{24}t))/(2R)$$
$$+ i\hat{U}_1^2(1,1,a)(B(\sin\lambda_{13}t + \sin\lambda_{14}t) + A(\sin\lambda_{23}t + \sin\lambda_{24}t))/(2R)$$

Table 1 continued

Table 1 (continued)

$$\begin{aligned}\mathcal{U}\hat{U}_0^2(1,1)\mathcal{U}^\dagger = &-\hat{U}_0^0(0,0)8\sqrt{2}\delta^2(1-\cos\lambda_{12}t)/(\sqrt{3}R^2)\\ &+\hat{U}_0^0(1,1)\sqrt{2}(R^2-D^2-16\delta^2\cos\lambda_{12}t)/(6R^2)\\ &-\mathrm{i}\hat{U}_0^1(1,0,s)4\delta(\sin\lambda_{12}t)/(\sqrt{3}R)+\hat{U}_0^1(0,1,a)4D\delta(1-\cos\lambda_{12}t)/(\sqrt{3}R^2)\\ &+\hat{U}_0^2(1,1)(2R^2+D^2+16\delta^2\cos\lambda_{12}t)/(3R^2)\end{aligned}$$

$$\begin{aligned}\mathcal{U}\hat{U}_1^2(1,1,s)\mathcal{U}^\dagger = &-\mathrm{i}\hat{U}_1^1(1,0,s)\sqrt{2}\delta(\sin\lambda_{14}t-\sin\lambda_{24}t)/R-\hat{U}_1^1(1,0,a)\sqrt{2}\delta(\cos\lambda_{14}t-\cos\lambda_{24}t)/R\\ &-\mathrm{i}\hat{U}_1^1(0,1,s)\sqrt{2}\delta(\sin\lambda_{13}t-\sin\lambda_{23}t)/R+\hat{U}_1^1(0,1,a)\sqrt{2}\delta(\cos\lambda_{13}t-\cos\lambda_{23}t)/R\\ &-\hat{U}_1^1(1,1,s)(B(\cos\lambda_{13}t-\cos\lambda_{14}t)+A(\cos\lambda_{23}t-\cos\lambda_{24}t))/(2R)\\ &+\mathrm{i}\hat{U}_1^1(1,1,a)(B(\sin\lambda_{13}t+\sin\lambda_{14}t)+A(\sin\lambda_{23}t+\sin\lambda_{24}t))/(2R)\\ &+\hat{U}_1^2(1,1,s)(B(\cos\lambda_{13}t+\cos\lambda_{14}t)+A(\cos\lambda_{23}t+\cos\lambda_{24}t))/(2R)\\ &-\mathrm{i}\hat{U}_1^2(1,1,a)(B(\sin\lambda_{13}t-\sin\lambda_{14}t)+A(\sin\lambda_{23}t-\sin\lambda_{24}t))/(2R)\end{aligned}$$

$$\mathcal{U}\hat{U}_2^2(1,1,s)\mathcal{U}^\dagger = \hat{U}_2^2(1,1,s)\cos\lambda_{34}t+\mathrm{i}\hat{U}_2^2(1,1,a)\sin\lambda_{34}t$$

$\mathcal{U}=\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar}$, $R=(D^2+16\delta^2)^{1/2}$,
$\lambda_{12}=-\frac{1}{2}R$, $\lambda_{13}=\Delta\bar{\omega}-\frac{1}{4}(2D+R)$,
$\lambda_{14}=-\Delta\bar{\omega}-\frac{1}{4}(2D+R)$, $\lambda_{23}=\Delta\bar{\omega}-\frac{1}{4}(2D-R)$,
$\lambda_{24}=-\Delta\bar{\omega}-\frac{1}{4}(2D-R)$, $\lambda_{34}=-2\Delta\bar{\omega}$,
$A=\frac{1}{2}(R-D)$, $B=\frac{1}{2}(R+D)$.

The underlying reason for dropping the scalar term in eq. (10) is a little elusive. If the chemical shift difference $\delta\to 0$, then eq. (6) reduces to

$$\mathcal{H}=\hbar\sqrt{2}\Delta\bar{\omega}\hat{U}_0^1(1,1)+\frac{\sqrt{6}}{4}D\hat{U}_0^2(1,1)\,, \tag{12}$$

which is block-diagonal in $I=1$. Thus the spin $I=1$ state is totally decoupled from the spin $I=0$ state. As a result we can treat the spin system as a simple $I=1$ system, because no admixing occurs between the $I=0$ and $I=1$ spin states available to the system. Consequently, the $\mathbf{I}_1\cdot\mathbf{I}_2$ scalar term appearing in eq. (10) is simply a constant and can be safely ignored.

In this paper no such approximations have been made other than that of the secular approximation. Thus table 1 can be used to obtain results for the two cases discussed above, simply by setting $\delta>>D$ for dissimilar spins and $\delta<<D$ for similar spins.

Using table 1 it is easy to show that following a $\pi/2$ pulse, the Fourier transformed NMR frequencies are given by

$$\lambda_{14}=\pm[\Delta\bar{\omega}+D/2+R/4]\,,$$

$$\lambda_{24}=\pm[\Delta\bar{\omega}+D/2-R/4]\,,$$

$$\lambda_{23}=\pm[\Delta\bar{\omega}-D/2+R/4]\,,$$

$$\lambda_{13} = \pm[\Delta\bar{\omega} - D/2 - R/4]\,, \tag{13}$$

where

$$R = \sqrt{D^2 + 16\delta^2}\,. \tag{14}$$

These frequencies are similar to but not identical with those of $\mathcal{H}_{ul}$ (9):

$$\Lambda_{14} = \pm[\Delta\bar{\omega} + D/2 + \delta]\,,$$

$$\Lambda_{24} = \pm[\Delta\bar{\omega} + D/2 - \delta]\,,$$

$$\Lambda_{23} = \pm[\Delta\bar{\omega} - D/2 + \delta]\,,$$

$$\Lambda_{13} = \pm[\Delta\bar{\omega} - D/2 - \delta]\,. \tag{15}$$

In the case of heteronuclear spins $\delta >> D$ and so $R \rightarrow 4\delta$. Thus eq. (13) converges to eq. (15), as expected. For homonuclear spins $\delta << D$, and so $R \rightarrow D$. In this case (i) the magnitudes of the terms associated with the λ_{24} and λ_{23} NMR frequencies vanish, and (ii) the difference between $\lambda_{14} - \lambda_{13}$ is found to be 3/2 times greater than that of $\Lambda_{14} - \Lambda_{13}$, as expected.

Note that when δ is non-zero, admixing will take place between the spin 0 and 1 states available to the system. Thus the NMR frequencies are not determined by the dipole–dipole coupling strength $(3/2)D$, but rather by $D/2 + \sqrt{D^2 + 16\delta^2}/4$. In addition, it should be noted that the chemical shift and dipolar terms in eq. (10) no longer commute with each other. Thus conclusions drawn using simplified evolution tables, based on eq. (11), will almost certainly be in error. This comment however does not apply to table 1 which covers both extremes discussed above and all the cases in between.

4. Discussion

As mentioned earlier, unit spherical tensors provide a good basis set for the description of multi-spin systems, because of their superior mathematical properties. However it should be acknowledged that in order to use the projection formula of (8), it is necessary to know the eigenfunctions and eigenvalues of the Hamiltonian in question. For three or more spins, some exact solutions are available in the literature. The case of three spin-1/2 nuclei has been examined by [5,6], four spin-1/2 nuclei by [7], five spin-1/2 by [8] and for six spin-1/2 nuclei by [9]. In general, such solutions are only possible if the spin system in question is highly symmetric.

It goes without saying that the preparation of evolution tables for three or more spins presents a formidable problem because the number of unit spherical tensors available to the spin system increases rapidly as more spins are added to the system. Nevertheless, if the exact eigenfunctions and eigenvalues are known, algebraic computer programs such as *Mathematica* can be used in conjunction with the projection formula of (8) to detail the evolution of a spin system. A general programme for this purpose is available upon request.

References

[1] G.J. Bowden, J.P.D. Martin and F. Separovic, Mol. Phys. 70 (1990) 581.
[2] B.C. Sanctuary, Mol. Phys. 55 (1985) 1017.
[3] R.R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon Press, Oxford, 1990).
[4] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
[5] E.R. Andrew and R. Bersohn, J. Chem. Phys. 18 (1950) 159.
[6] J.S. Waugh, F.B. Humphrey and D.M. Yost, J. Phys. Chem. 57 (1953) 486.
[7] R. Bersohn and H.S. Gutowsky, J. Chem. Phys. 22 (1954) 651.
[8] R. Blinc, Z. Trontelj and B. Volavšek, J. Chem. Phys. 44 (1966) 1028.
[9] A.M. Panich, J. Magn. Reson. 66 (1986) 9.