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Multipole N.M.R.
XII. Theory of spin decoupling

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Using a two-spin multipole formulation, spin decoupling is analysed analytically from arbitrary initial spin preparations. The rotating frame which is most convenient is $\bar{\omega} \equiv \frac{1}{2}(\omega_{01} + \omega_{02})$ rather than the commonly used Larmor frequency of the irradiated spin ω_{02}. The importance of unobserved polarizations (bilinear operators) is stressed by identifying these terms as providing pathways to spin coupling which must be destroyed for decoupling. Appropriate linear combinations of the bilinear polarizations can be rotated by the perturbing field. Some general observations of the effects of periodic pulse sequences and amplitude modulation are included.

1. INTRODUCTION

Spin decoupling has become an indispensible technique which leads to simplification and narrowing of coupled N.M.R. spectra. Early experimental work showed [1] its utility by making use of double resonance irradiation. Solids [2–5], liquid crystals [6, 7], and liquids [8, 9] have all been demonstrated to have similar consequences resulting from perturbing one spin with an rf field. The theory used to describe spin decoupling has been limited, almost exclusively, to diagonalizing the hamiltonian and calculating the various transition probabilities. Furthermore, following the early calculations [1], a rotating frame at the perturbing rf frequency is usually evoked, as well as truncating the coupling hamiltonian to $JI_{1z}I_{2z}$.

By solving the problem in the above described way, the situation in mind is that of cw double resonance experiments. Today this is rarely done, being superceded by a great variety of pulses with phase and amplitude modulation particularly in broadband decoupling [10–13]. A detailed theoretical treatment of pulsed decoupling sequences, however, should be able to follow the full spin density matrix throughout the duration of the pulse sequence. In the final FID the nuclear magnetization, which is a particular linear combination of single quantum transitions, is observed and the actual spectrum depends critically on the past history of state preparation. Usually a full density matrix treatment is not given although recent theory shows [10] one can approximately describe pulse sequences as a product of unitary transformations on the initial density matrix, use being made of average hamiltonian theory [14].

The importance of calculating all the polarizations in the system is readily

seen by deuterium spin decoupling, first suggested by Meiboom [7] and exploited by Pines *et al.* [2–4]. By irradiating the double quantum transition and using perturbation theory, they show that decoupling can be accomplished using lower rf power than if the single quantum lines are irradiated. This opens up a whole range of multiquantum experiments which may lead to low rf power decoupling.

In recent years a great deal of attention has been paid to broadband decoupling by attempting to devise pulse sequences which correct for pulse imperfections, and devise specific pulses on spins far off resonance as if they were on resonance. Such problems are not the motivation of this work. Rather we treat the problem as one of locating what we call the pathway to spin coupling, with applications to both solids and liquids in mind for later applications of our theory.

The above discussion points out two areas which need theoretical development. Firstly it is necessary to have a theory which allows the RID to be calculated after any pulse sequence from any initial condition. Secondly the effects of multiquantum excitation on spin decoupling should be formulated. One approach used for the second has been the fictitious spin [15–16] and related [17, 18] bases whereby the higher, bi- and multilinear, operator are included in the spin dynamics. Another basis are those Bain calls superspin [19] which are reviewed in paper XI of this series [20].

In this paper the above two areas are discussed within the multipole framework. The full density matrix is calculated for general initial conditions, giving not only analytic results, but also a form which is readily treated numerically.

As a first example of spin decoupling, the case of two scalar coupled spins of 1/2 in the presence of a perturbing field is treated; the AX system. Although studied extensively [21], no exact analytic solution to the full density matrix existed until now. In our treatment the full scalar coupling term $J\mathbf{I}_1\cdot\mathbf{I}_2$ is retained since the dot product, $\mathbf{I}_1\cdot\mathbf{I}_2$, is a naturally occurring multipole operator. It is proportional to $T^{00}(11)$, a scalar bilinear operator which is simply treated in the multipole approach. In contrast, the truncated form, $I_{1z}I_{2z}$, although easier to work with when operating on a product basis $|I_1M_1I_2M_2\rangle$, has in fact, second rank tensor components (see (11) of paper XI [20]). On the other hand, we cannot irradiate, say spin 2, without affecting spin 1 in an AB system. Consequently after obtaining the equations using $J\mathbf{I}_1\cdot\mathbf{I}_2$, we ignore terms in the limit $|\omega_D| \equiv |1/2(\omega_{01} - \omega_{02})| \gg J/2$ leading to results valid for the AX system.

Moreover, in contrast to other treatments, we use a rotating frame which is at the average larmor frequency $\bar{\omega} = 1/2(\omega_{01} + \omega_{02})$ rather than that at the perturbed spin frequency ω_{02}. Although this means the perturbing field is not stationary, no difficulties are encountered in the multipole basis since the polarizations are simply rotated. An advantage of this frame is the symmetry introduced between the two spins, namely the J splittings are equally spaced about $\bar{\omega} \pm \omega_D$.

In this problem, the double quantum coherence is uncoupled from the single quantum coherences in contrast to the deuterium problem [2–4]. There exists, however, a bilinear operator which contains two frequencies, namely ω_{01} and ω_{02} (or in the $\bar{\omega}$ frame at $\pm\omega_D$). This operator transforms like the vector cross product and as such is perpendicular to both spin 1 and spin 2 vectors. The two frequencies of the vector cross product provide the only pathway through which the two spins can couple. Spin decoupling is accomplished if this pathway can be destroyed. As the rf power increases, at or near the spin 2 resonance, both the vector $\mathbf{I}_2$ and the vector cross product $\mathbf{I}_1 \times \mathbf{I}_2$ are rotated by the rf field in

essentially the same way. It is the rotation of the vector cross product induced by the rf perturbation which reduces the coupling strength J as well as introducing additional satellites. Hence, in this picture, irradiating at ω_{02} excites bilinear operators.

After treating the two scalar coupled spin case, a general treatment of rotation of multilinear operators is given. This is based on the idea that there always exists in the coupled system, a set of operators which contain frequencies which simultaneously provide a resonance coupling between nuclear spins. A technique is given to identify these operators. Once known, the spins which have a Larmor frequency in common with the frequencies of the multilinear polarization can be uncoupled by irradiating at one, or several, of the frequencies. Such a frequency may differ from the actual Larmor frequencies of the spins to be decoupled, as in the case of deuterium decoupling when the double quantum line is irradiated.

2. Basis for decoupling

A multipole basis is convenient for evaluating the matrix elements, and also for organizing the spin transition probabilities into rotationally invariant polarizations which are kth rank tensors $\phi^k(k_1k_2)$ [20, 21]. For spins of 1/2, experiment measures the single quantum components of either spin 1, $\phi^1_{\pm 1}(10)$ or spin 2, $\phi^1_{\pm 1}(01)$, while all other polarizations depend upon products of spin operator, e.g. proportional to $\mathbf{I}_1\mathbf{I}_2$, the so-called bilinear operators. The spectrum of these operators, as discussed above, is needed to find the coupling pathway. In order to identify the modes of the bilinear operator which couple the spins, the full density matrix is diagonalized at first in the *absence* of any r.f. field and with $J = 0$. This is usually very easy. In the case at hand, from (21) and (33) of [20], it is seen that $\phi^1_q(10)$, $\phi^1_q(01)$ and $\phi^2_{\pm 2}(11)$ are already diagonal while a 2×2 block in (21) of [20] and a 3×3 block in (33) of [20] diagonalize with the following definitions,

$$\chi^{\pm}_q(11) = \pm \frac{1}{\sqrt{2}} [\phi^1_q(11) \pm \phi^2_q(11)], \quad q = \pm 1, \tag{1}$$

$$\chi^{\pm}_0(11) = \frac{1}{\sqrt{3}} \left[\phi^0_0(11) \pm \sqrt{\tfrac{3}{2}}\, \phi^1_0(11) + \frac{1}{\sqrt{2}}\, \phi^2_0(11) \right], \tag{2}$$

$$\chi^0_0(11) = -\frac{1}{\sqrt{3}} [\phi^0_0(11) - \sqrt{2}\, \phi^2_0(11)]. \tag{3}$$

The advantage of this basis is that in the presence on an r.f. field, different linear combinations can be rotated like vectors. Other bases [3, 4, 10], discussed in paper XI, do not have this property.

The r.f. hamiltonian is taken as being close to the spin 2 resonance with the form,

$$\begin{aligned} \mathscr{H}_{\text{r.f.}}(t) &= -\gamma_2 \hbar \mathbf{I}_2 \cdot \mathscr{H}_1(t) \\ &= -\frac{\gamma_2 \hbar}{2} \sum_m \mathscr{T}^{(1)m}(\mathbf{I}_2) H_m(t), \end{aligned} \tag{4}$$

where

$$H_{\pm 1}(t) = \pm \frac{i}{\sqrt{2}}\, h_{\pm}(t) \exp [\pm i(\omega t - \phi)], \; H_0 \equiv 0 \tag{5}$$

which contains an arbitrary phase shift ϕ. The r.f. amplitude $h_{\pm}(t)$ can be any function of time and

$$\omega_{\pm 1}(t) = \gamma_2 h_{\pm}(t). \tag{6}$$

Equations (4)–(6) ignore the r.f. irradiation on spin 1. This is only valid when $\omega_{01} \neq \omega_{02}$ and irradiation close to spin 2 resonance does not affect spin 1. It is straightforward to include the effects of r.f. on both spins, but we do not treat such a situation.

In the absence of J coupling, and assuming the observed spin 1 is not affected by $\mathscr{H}_{\text{r.f.}}(t)$, 12 of the 15 equations can be symmetrically arranged as

$$\frac{d}{dt}\begin{pmatrix} \hat{\phi}^1_1(01) \\ \hat{\phi}^1_0(01) \\ \hat{\phi}^1_{-1}(01) \end{pmatrix} = \begin{pmatrix} -i\omega_D & \gamma_2 H_1 & 0 \\ -\gamma_2 H_{-1} & 0 & \gamma_2 H_1 \\ 0 & -\gamma_2 H_{-1} & i\omega_D \end{pmatrix} \begin{pmatrix} \hat{\phi}^1_1(01) \\ \hat{\phi}^1_0(01) \\ \hat{\phi}^1_{-1}(01) \end{pmatrix}, \tag{7}$$

$$\frac{d}{dt}\begin{pmatrix} \hat{\phi}^2_2(11) \\ \hat{\chi}^+_1(11) \\ \hat{\chi}^+_0(11) \end{pmatrix} = \begin{pmatrix} 0 & \gamma_2 H_1 & 0 \\ -\gamma_2 H_{-1} & i\omega_D & \gamma_2 H_1 \\ 0 & -\gamma_2 H_{-1} & i2\omega_D \end{pmatrix} \begin{pmatrix} \hat{\phi}^2_2(11) \\ \hat{\chi}^+_1(11) \\ \hat{\chi}^+_0(11) \end{pmatrix}, \tag{8}$$

$$\frac{d}{dt}\begin{pmatrix} \hat{\chi}^-_0(11) \\ \hat{\chi}^-_{-1}(11) \\ \hat{\phi}^2_{-2}(11) \end{pmatrix} = \begin{pmatrix} -2i\omega_D & \gamma_2 H_1 & 0 \\ -\gamma_2 H_{-1} & -i\omega_D & \gamma_2 H_1 \\ 0 & -\gamma_2 H_{-1} & 0 \end{pmatrix} \begin{pmatrix} \hat{\chi}^-_0(11) \\ \hat{\chi}^-_{-1}(11) \\ \hat{\phi}^2_{-2}(11) \end{pmatrix}, \tag{9}$$

$$\frac{d}{dt}\begin{pmatrix} \hat{\chi}^-_{+1}(11) \\ \hat{\chi}^0_0(11) \\ \hat{\chi}^+_{-1}(11) \end{pmatrix} = \begin{pmatrix} -i\omega_D & \gamma_2 H_1 & 0 \\ -\gamma_2 H_{-1} & 0 & \gamma_2 H_1 \\ 0 & -\gamma_2 H_{-1} & i\omega_D \end{pmatrix} \begin{pmatrix} \hat{\chi}^-_{+1}(11) \\ \hat{\chi}^0_0(11) \\ \hat{\chi}^+_{-1}(11) \end{pmatrix}. \tag{10}$$

The rotating frame is defined by $\bar{\omega}$,

$$\hat{\xi}^k_q(t) = \exp(-iq\bar{\omega}t)\xi^k_q(t). \tag{11}$$

In the form (1)–(3) the operator basis is similar to that used in [23]. The reason for the usefulness of this basis lies in the components all being eigenfunctions of the Zeeman hamiltonian, and the fact that r.f. pulses simply rotate them (see § 3). When J coupling exists, then using the full scalar coupling, $J\mathbf{I}_1 \cdot \mathbf{I}_2$, in the absence of any magnetic field, gives terms which couple the 15 equations together according to

$$\frac{d\hat{\phi}^1_q(10)}{dt} = \frac{J}{2}[\hat{\chi}^+_q(11) - \hat{\chi}^-_q(11)], \tag{12}$$

$$\frac{d\hat{\phi}^1_q(01)}{dt} = -\frac{J}{2}[\hat{\chi}^+_q(11) - \hat{\chi}^-_q(11)], \tag{13}$$

$$\frac{d\hat{\chi}^{\pm}_q(11)}{dt} = \mp\frac{J}{2}\hat{\phi}^1_q(10) \pm \frac{J}{2}\hat{\phi}^1_q(01). \tag{14}$$

Equations (7)–(10) are valid when $J = 0$ and the r.f. is on, close to the spin 2 resonance. Equations (12)–(14) are the J contributions close to the spin 2 resonance. Equations (12)–(14) are the J contributions which cause polarization transfer. When $\mathscr{H}_{\text{r.f.}} = 0$ and the hamiltonian is the Zeeman and scalar coupling, the solutions are given in [20].

Apart from the r.f. contribution, the equations in this section are derived in paper [20]. The r.f. parts are obtained by similar techniques by substituting (4) for $\mathscr{H}_0$ in Appendix B of [20].

3. Rotation of the bilinear operations for $J = 0$

From (7)–(10) it can be seen that the r.f. applied close to the resonance of the second spin has the same off-diagonal form. The diagonal elements are different indicating that each component, relative to the $\bar{\omega}$ frame, precesses at multiples of $\pm\omega_D$. It is possible to transform each of (7)–(10) to be identical to equations (49)–(51) of [24] the solutions then being given for constant $\omega_1(t) = \omega_1$ for (7) by

$$\hat{\phi}^1_q(01)[t] = \sum_{q'} \mathscr{D}^1_{qq'}(\Omega)\phi^1_{q'}(01)[0], \tag{15}$$

for (8) by

$$\hat{\xi}^+_{q+1}(11)[t] = \exp(i\omega_D t) \sum_{q'} \mathscr{D}^1_{qq'}(\Omega)\xi^+_{q'+1}(11)[0], \tag{16}$$

for (9) by

$$\hat{\xi}^-_{q-1}(11)[t] = \exp(-i\omega_D t) \sum_{q'} \mathscr{D}^1_{qq'}(\Omega)\xi^-_{q'-1}(11)[0] \tag{17}$$

and for (10) by

$$\hat{\xi}^0_q(11)[t] = \sum_{q'} \mathscr{D}^1_{qq'}(\Omega)\xi^0_q(11)[0], \tag{18}$$

where the sets are ($q = \pm 1, 0$)

$$\hat{\xi}^+_{q+1}(11) = \{\hat{\phi}^2_2(11), \hat{\chi}^+_1(11), \hat{\chi}^+_0(11)\}, \tag{19}$$

$$\hat{\xi}^-_{q-1}(11) = \{\hat{\chi}^-_0(11), \hat{\chi}^-_{-1}(11), \hat{\phi}^2_{-2}(11)\} \tag{20}$$

and

$$\hat{\xi}^0_q(11) = \{\hat{\chi}^-_{+1}(11), \hat{\chi}^0_0(11), \chi^+_{-1}(11)\} \tag{21}$$

corresponding to (16)–(18) respectively. The Wigner rotation matrices, $\mathscr{D}$, are those of Edmonds [25] and the angles Ω are

$$\Omega = (\alpha + \phi, \beta, \alpha - \phi - \omega_D t + \Delta\omega t + \pi), \tag{22}$$

with

$$\cos\beta = \frac{1}{\Omega^2}[\Delta\omega^2 + \omega_1^2 \cos\Omega t], \tag{23}$$

where

$$\tan\alpha = \frac{\Omega}{\Delta\omega} \operatorname{cotan}(\Omega t/2), \tag{24}$$

$$\Omega = \sqrt{(\Delta\omega^2 + \omega_1^2)} \tag{25}$$

and

$$\Delta\omega = \omega - \bar{\omega} + \omega_D = \omega - \omega_{02}. \tag{26}$$

The solutions (15)–(18) show that, in addition to the usual picture of a pulse on resonance with spin 2 causing the vector $\mathbf{I}_2 \propto \boldsymbol{\phi}^1(01)$ to be rotated, there exists 3 other vector quantities, $\boldsymbol{\xi}^{\pm}$, $\boldsymbol{\xi}^0$ which are also resonantly rotated. The vector $\phi_q^1(01)$ moves between the z and x, y laboratory axis, a process which is equivalent to changing zero quantum to single quantum coherences. The vector $\hat{\xi}_{q+1}^{+}$ and $\hat{\xi}_{q-1}^{-}$ exchange double, single and zero quantum while $\hat{\xi}_q^0$ changes zero and single quantum coherences of the bilinear polarizations. In the absence of any spin coupling, these motions occur independently. Moreover, if only $\phi_q^1(01)$ or $\phi_q^1(10)$ polarization is initially present, none of this can be transferred to the bilinear operator and consequently the motions of ξ_q^p do not occur. J coupling changes this.

It is useful to view these motions in the Laplace space, s, using

$$\Phi(s) = \int_0^{\infty} \exp(-st)\phi(t)\, dt \equiv \mathscr{L}_T[\phi(t)]. \tag{27}$$

Consider the case of three coupled equations similar to (7)–(10),

$$\frac{d}{dt}\begin{pmatrix}\phi_1(t)\\ \phi_0(t)\\ \phi_{-1}(t)\end{pmatrix} = \frac{i}{\sqrt{2}}\begin{pmatrix} 0 & \omega_{+1}(t)\exp[i(\Delta\omega t-\phi)] & 0\\ +\omega_{-1}(t)\exp[-i(\Delta\omega t-\phi)] & 0 & \omega_{+1}(t)\exp[i(\Delta\omega t-\phi)]\\ 0 & +\omega_{-1}(t)\exp[-i(\Delta\omega t-\phi)] & 0\end{pmatrix}\begin{pmatrix}\phi_1(t)\\ \phi_0(t)\\ \phi_{-1}(t)\end{pmatrix}, \tag{28}$$

where the diagonal frequencies have been transformed away. In the case that $\omega_{\pm}(t) = \omega_{\pm 1}$, a constant amplitude, the Laplace transform of (28) yields

$$\Phi_q(s) = \sum_{q'} D_{qq'}^1(s)\Phi_{q'}(0), \tag{29}$$

where $D_{qq'}^1(s)$ is the Laplace transform of $\mathscr{D}_{qq'}^1(\Omega)$. The table lists the matrix elements of $D_{qq'}^1(s)$ which are functions of $\Delta\omega$, ω_1 and ϕ just as is $\mathscr{D}_{qq'}^1(\Omega)$.

4. *AX* SPIN DECOUPLING

To treat the combined effects of r.f. irradiation on spin 2, the 12 equations (12)–(14) for J coupling, the 12 equations (7)–(10) for r.f. irradiation and the 3 equations for the observed spin 1 $\phi_q^1(10)$ are combined. In Laplace space, the observed spin is governed by

$$(s - iq\omega_D)\hat{\Phi}_q^1(10)[s] = \phi_q^1(10)[0] + \frac{J}{2}\{\hat{\chi}_q^+(11)[s] - \hat{\chi}_q^-(11)[s]\}. \tag{30}$$

To obtain the equations for the irradiated spin, we now assume that $\omega_D^2 \gg J^2/2$. This approximation has the effect of eliminating rotational coupling between the bilinear operators and the irradiating spin which correspond to different multiquantum coherences. That is, terms containing $J^2/2D'_{qq'}(s)$ with $q \neq q'$ drop out in this approximation. The equations governing the irradiated spin becomes,

$$\hat{\Phi}_q^1(01)[s - iq\omega_D] = \sum_{q'} D_{qq'}^1(s)\phi_{q'}^1(01)[0] - \frac{J}{2} D_{qq}^1(s) \times \{\hat{\chi}_q^+(11)[s - iq\omega_D] - \hat{\chi}_q^-(11)[s - iq\omega_D]\}. \tag{31}$$

The Laplace transform of the Wigner rotation matrix $\mathscr{D}^1_{qq'}(\alpha + \phi, \beta, \alpha - \phi + \Delta\omega t + \pi)$.

$\frac{1}{s}\left\{1 - \frac{\omega_1^2}{2}\frac{s - i2\,\Delta\omega}{(s - i\,\Delta\omega)[(s - i\,\Delta\omega)^2 + \Omega^2]}\right\}$,	$\frac{i\omega_1 \exp(-i\phi)}{\sqrt{2}\,s}\left\{\frac{(s - i\,\Delta\omega)^2 + \Delta\omega^2}{(s - i\,\Delta\omega)[(s - i\,\Delta\omega)^2 + \Omega^2]}\right\}$,	$\frac{-\omega_1^2 \exp(-i2\phi)}{2}\left\{\frac{1}{(s - i\,\Delta\omega)[(s - i\,\Delta\omega)^2 + \Omega^2]}\right\}$
$\frac{i\omega_1 \exp(i\phi)(s - i\,\Delta\omega)}{\sqrt{2}\,s(s^2 + \Omega^2)}$	$\frac{1}{s}\left[\frac{s^2 + \Delta\omega^2}{s^2 + \Omega^2}\right]$	$\frac{i\omega_1 \exp(-i\phi)(s + i\,\Delta\omega)}{\sqrt{2}\,s(s^2 + \Omega^2)}$
$-\frac{\omega_1^2 \exp(i2\phi)}{2}\frac{1}{(s + i\,\Delta\omega)[(s + i\Delta\omega)^2 + \Omega^2]}$	$\frac{i}{s}\frac{\omega_1 \exp(i\phi)}{\sqrt{2}}\left\{\frac{(s + i\,\Delta\omega)^2 + \Delta\omega^2}{(s + i\,\Delta\omega)[(s + i\,\Delta\omega)^2 + \Omega^2]}\right\}$	$\frac{1}{s}\left[1 - \frac{\omega_1^2(s + 2i\,\Delta\omega)}{2(s + i\,\Delta\omega)[(s + i\,\Delta\omega)^2 + \Omega^2]}\right]$

As the r.f. power increases, the first term, which is just a rotation, dominates the second. The second term can lead to transferring polarization to spin 1 from spin 2. We retain both terms below.

Recall from (1) that the combination $\chi^+ - \chi^-$ is a bilinear function. Although these two equations are still coupled via J, the irradiated spin has its coupling modified to $JD^1_{qq}(s)$. The remaining polarizations (19)–(21), ξ^p_q, $p = 0, \pm 1$ are governed by

$$\Xi^{\pm 1}_{q\pm 1}(11)[s^- i\omega_D(q_+ \pm 1)] = \sum_{q'} D^1_{qq'}(s)\xi^{\pm}_{q'\pm 1}(11)[0] \mp \frac{J}{2} D^1_{qq}(s)\hat{\Phi}^1_{q\pm 1}(10)[s^- i\omega_D(q_+ \mp 1)] \pm \frac{J}{2} D^1_{qq}(s)\hat{\Phi}^1_{q\pm 1}(01)[s^- i\omega_D(q_+ \mp 1)] \tag{32}$$

and

$$\Xi^0_q(11)[s - i\omega_D q] = \sum_{q'} D^1_{qq'}(s)\xi^0_{q'}(11)[0] + q\frac{J}{2} D^1_{qq}(s)\hat{\Phi}^1_q(10)[s - i\omega_D q] - q\frac{J}{2} D^1_{qq}(s)\hat{\Phi}^1_q(01)[s - i\omega_D q]. \tag{33}$$

The Laplace transform of ξ^p is Ξ^p.

These 15 algebraical equations can be solved exactly. Since the xy magnetization of spin 1 is experimentally studied, only $\phi^1_1(10)[t]$ is presented here. The difference

$$\hat{\chi}^+_1(11)[s] - \hat{\chi}^-_1(11)[s] = \mathscr{D}^1(s - i\omega_D, s + i\omega_D) - \frac{J}{2}[D^1_{00}(s - i\omega_D) + D^1_{11}(s + i\omega_D)][\hat{\Phi}^1_1(10)[s] - \Phi^1_1(01)[s]], \tag{34}$$

where

$$\mathscr{D}^1(s - i\omega_D, s + i\omega_D) \equiv \sum_{q'} D^1_{0q'}(s - i\omega_D)\xi^+_{q'+1}(11)[0] - \sum_{q'} D^1_{1q'}(s + i\omega_D)\xi^0_{q'}(11)[0] \tag{35}$$

is substituted into (31). The result is

$$\hat{\Phi}^1_1(10)(s) = \frac{1}{R(s - i\omega_D)}\left\{\left[1 + \frac{J^2}{4}(D^1_{00}(s - i\omega_D) + D^1_{11}(s + i\omega_D))D^1_{11}(s + i\omega_D)\right]\phi^1_1(10)(0) + \frac{J}{2}\mathscr{D}^1(s - i\omega_D, s + i\omega_D) + \frac{J^2}{4}[D^1_{00}(s - i\omega_D) + D^1_{11}(s + i\omega_D)]\sum_{q'} D^1_{1q'}(s + i\omega_D)\hat{\phi}^1_{q'}(01)(0)\right\}, \tag{36}$$

where the resolvent is

$$R(s - i\omega_D) = s - i\omega_D + J^2_{eff}(s). \tag{37}$$

The effective coupling constant is now s dependent being

$$J^2_{eff}(s) = \frac{J^2}{4}[D^1_{00}(s - i\omega_D) + D^1_{11}(s + i\omega_D)][1 + (s - i\omega_D)D^1_{11}(s + i\omega_D)]. \tag{38}$$

Equation (36) may appear involved, but note that it contains all possible initial conditions. In most treatments usually only $\phi^1_1(10)[0]$ is retained. The roots of the resolvent give simple poles when (37) is inverted. Each pole corresponds to a specific eigenfrequency of the system.

The simplest case, and a check on the expression, arises when $\omega_1 = 0$ whence the resolvent becomes,

$$\frac{1}{R(s - i\omega_D)} = \frac{(s^2 + \omega_D^2)(s + i\omega_D)}{(s^2 + \omega_D^2)^2 + s^2J^2}. \tag{39}$$

The four roots are just

$$\lambda_{\pm 2} = \pm\frac{J}{2} \pm \frac{1}{2}\sqrt{(4\omega_D^2 + J^2)}, \tag{40}$$

$$\lambda_{\pm 1} = \mp\frac{J}{2} \pm \frac{1}{2}\sqrt{(4\omega_D^2 + J^2)}, \tag{41}$$

being the usual eigenfrequencies relative to $\bar{\omega}$. We note also that the same result obtains when the r.f. is far from resonance, $|\Delta\omega| \gg \omega_1$, as expected.

For $|\Delta\omega| \sim \omega_1$ a number of frequencies occur whose origins are the precessions arising from the rotation matrices. The intensities associated with these are mostly small and have been numerically studied elsewhere [8].

The structure of J^2_{eff} in (38) reveals the frequency spectrum of the resolvent, (37). Consider the case when the roots about spin 1 are of interest and spin 2 is resonantly irradiated. In this case $s \cong i(\omega + \delta)$ where δ is small. As such, only $D^1_{00}(s - i\omega_D)$ is large while $D^1_{11}(s + i\omega_D)$ terms can be neglected. The resolvent becomes

$$R(s - i\omega_D) \cong s - i\omega_D + J^2/4D^1_{00}(s - i\omega_D) \tag{42}$$

and the frequencies are then given by

$$s_0 = i\omega_D \tag{43}$$

and

$$s_\pm = i\omega_D \pm i\sqrt{[J^2/4 + \omega_1^2]}. \tag{44}$$

Study of the residues shows that as ω_1^2 increases, the J splitting about ω_D decreases in intensity and moves out away from ω_D. At the same time a central line grows at ω_D showing spin decoupling effects as ω_1 increases [8]. One is left with

$$\phi^1_1(10)[t] = \exp(i\omega_{01}t)\phi^1_1(10)[0] \tag{45}$$

in the large ω_1 limit. We can, however, evaluate the other contributions which arise when other initial polarizations, such as bilinear, are produced. Note that no

term $\phi_0^1(10)[0]$ exists in (36) indicating that an initial 90° pulse on the observed spin is required before the decoupling is applied. The same restriction is not imposed on the second spin which can be irradiated at equilibrium.

The frequencies about the irradiated spin 2 can also be studied from (37)–(38) but we omit the details except to note that in this case $D_{11}^1(s + i\omega_D)$ dominates (38) and that the term, $(s - i\omega_D)D_{11}^1(s + i\omega_D)$ arises from the second term in (31) which, becomes small as ω_1 increases.

The expression for J_{eff}, (38) is similar in physical content to Waugh [10]. In his theory he notes that J is scaled down when average hamiltonian theory is used. In fact, apart from the use here of the full $J\mathbf{I}_1 \cdot \mathbf{I}_2$ term, the models of Waugh's and here are identical. Differences occur in the theoretical treatments. In Waugh's case he remains in the time domain and calculates the approximate scaling down of J as a series. By going into Laplace domain, we have extended this to obtain the exact scaling functions for AX systems (38), valid off-resonance in terms of physically relevant parameters, namely rotation matrices. Moreover, from (36), the FID can be obtained analytically from any initial condition.

Emerging from this treatment of two spin decoupling is the physical picture which rests on identifying and calculating the role of the bilinear operators which provide the pathway for coupling, and which irradiation destroys. In this case the quantities $\chi_q^{\pm}(11)$ have only two frequencies at, ω_{01} and ω_{02}, but more complicated coupled spin clusters doubtless have additional frequencies which can lead to more efficient destruction of the coupling pathway.

5. General effects of irradiation

In the two coupled spin case, 3 vectors (7)–(10), are identified as being rotated by a near resonance irradiation of spin 2. In a general situation of N spins coupled by any mechanisms, the first step is to calculate the strongly coupled natural frequencies in the system. By strongly coupled, it is meant those terms in the hamiltonian which cannot be decoupled by an r.f. field. Once identified, the application of an r.f. field causes certain of the systems polarizations to be rotated. Finally the weakly coupled hamiltonian, that part to be decoupled, is treated, usually as a perturbation.

In this section it is assumed that the multilinear operators have been identified, and the question then arises as to the effects of pulses, pulse sequences and amplitude modulation on these operators or associated polarizations. The equation governing r.f. irradiation of such polarizations in the absence of couplings can be written as a generalization of (28) as

$$\frac{\partial \hat{\phi}_q^k(t)}{\partial t} = \frac{i\omega_{+1}(t)}{2} \exp\,(i(\Delta\omega t - \phi))\sqrt{[(k+q)(k-q+1)]}\hat{\phi}_{q-1}^k(t)$$

$$+ \frac{i\omega_{-1}(t)}{2} \exp\,(-i(\Delta\omega t - \phi))\sqrt{[(k-q)(k+q+1)]}\hat{\phi}_{q+1}^k(t). \quad (46)$$

Equations (7)–(10) are examples of this for $k = 1$. For convenience a rotating frame has been chosen which puts the diagonal frequency terms $iq\omega_0$ into the exponential as an off-resonance factor. The amplitudes are taken to be time dependent.

The Laplace transform of (46) is

$$s\Phi_q^k(s + iq\omega_0) = \phi_q^k(0) + \frac{1}{4\pi}\sqrt{[(k+q)(k-q+1)]}\exp(-i\phi)\int_{c-i\infty}^{c+i\infty}\bar{\omega}_{+1}(u) \times \phi_{q-1}^k(s - u + i(q-1)\omega_0 - i\,\Delta\omega)\,du + \frac{1}{4\pi}\sqrt{[(k-q)(k+q+1)]}\exp(i\phi)\int_{c-i\infty}^{c+i\infty}\bar{\omega}_{-1}(u)\phi_{q+1}^k \times (s - u + i(q+1)\omega_0 + i(\Delta\omega))\,du. \quad (47)$$

where $\bar{\omega}_i(u)$ is the Laplace transform of $\omega_i(t)$.

(i) *Constant amplitude, ω_1*

In the case that ω_1 is time independent $\bar{\omega}_{\pm 1}(u) = (\omega_1/u)$ and (47) reduces to

$$\Phi_q^k(s + iq\omega_0) = \sum_{q'} D_{qq'}^k(s)\phi_{q'}(0) \quad (48)$$

of which (29) is an example, and $D_{qq'}^k(s)$ is the Laplace transform of $\mathscr{D}_{qq'}^k(\Omega)$.

(ii) *Resonance solution for general $\omega_{\pm 1}(t)$*

If $\Delta\omega = 0$, it is a simple matter to exactly solve (46) for any amplitude modulation $\omega_1(t) = \omega_{-1}(t)$. The solution is formally the same as (48) or the inverse,

$$\phi_q^k(t) = \exp(iq\omega_0 t)\sum_{q'}\mathscr{D}_{qq'}^k\left(+\phi - \frac{\pi}{2},\ \beta(t),\ \frac{\pi}{2} - \phi - \omega_D t\right)\phi_{q'}^k(0), \quad (49)$$

where

$$\beta(t) \equiv \int_0^t \omega_1(t)\,dt \quad (50)$$

for a pulse of duration t.

(iii) *Off-resonance solutions for general $\omega_{\pm 1}(t)$*

Consider a general time dependent amplitude which can be analyzed in a Fourier series,

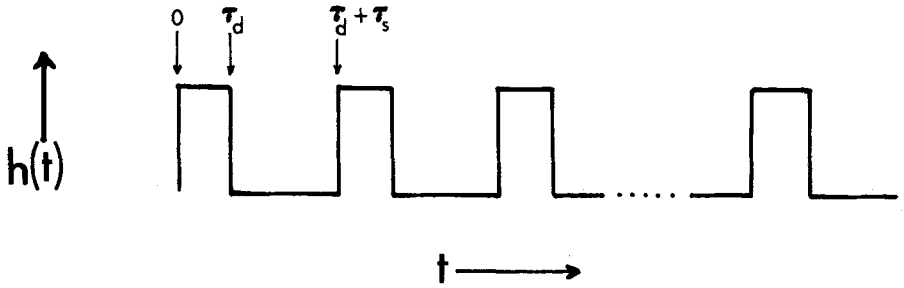
$$\omega_{\pm 1}(t) = \sum_{n=-\infty}^{\infty} a_n \exp(\mp i\omega_n t). \quad (51)$$

Substitution into (46) gives

$$\frac{\partial\hat{\phi}_q^k(t)}{\partial t} = \frac{i}{2}\sum_{n=-\infty}^{\infty} a_n \exp[i(\Delta\omega t - \omega_n t - \phi)]\sqrt{[(k+q)(k-q+1)]}\hat{\phi}_{q-1}^k(t) + \frac{i}{2}\sum_{n=-\infty}^{\infty} a_n \exp[-i(\Delta\omega t - \omega_n t - \phi)]\sqrt{[(k-q)(k+q+1)]}\hat{\phi}_{q+1}^k(t). \quad (52)$$

Amplitude modulation by a single frequency ω_m is a special case of (51) whence

$$\omega_{\pm 1}(t) = a_m \exp(\mp i\omega_m t). \quad (53)$$



A comb of pulses of width τ_d and spacings τ_s.

The Fourier components are seen to shift the resonance conditions from $\omega = \omega_0$ off-resonance to the positions $\omega = \omega_0 \pm \omega_n$.

It can be shown that the effects of the rotation matrices are small when calculated off-resonance, or when $|\omega - \omega_n| \gg 0$. Only those Fourier components are effective when $|\omega - \omega_n| \sim 0$. This reduces to the simple constant-amplitude rotation case of the whole frequency bands if there are enough fourier components close to the natural frequencies.

(iv) *Comb of pulses*

Many possible pulse sequences exist ([26–30]) which are often used empirically. Consider the case of a comb of pulses all of the same amplitude h_1 and closely spaced (figure) of duration τ_d and of equal separation τ_s. Mathematically this is given by

$$h_{\pm 1}(t) = h_1 \begin{cases} 1 & \text{if } n(\tau_d + \tau_s) < t < n(\tau_d + \tau_s) + \tau_d, \\ 0 & \text{if } n(\tau_d + \tau_s) + \tau_d < t < (n+1)(\tau_d + \tau_s). \end{cases} \tag{54}$$

Although such a sequence is discontinuous in the time domain, it is periodic. Consequently it is a natural candidate for the Laplace transform, whereby this particular amplitude modulation becomes

$$\bar{\omega}_1(s) = \gamma h_1(s) = \omega_1 \left[\frac{1 - \exp(-\tau_d s)}{s(1 - \exp(-\tau_s s - \tau_d s))} \right]. \tag{55}$$

On the other hand, the Laplace transform of a great variety of different shapes and amplitudes are available [31]. When the amplitude is not constant, the convolution in Laplace space (47) is the price paid for a simple Laplace function for a periodic pulse sequence. On the other hand, from the above discussion (iii) only those poles which are close to natural frequencies need be included in the calculation. For the comb in figure 1, the poles of $\bar{\omega}_1(s)$ are $s = 0$ and

$$s = \frac{2\pi i n}{(\tau_s + \tau_d)}, \tag{56}$$

where n is a positive or negative integer. Hence a broader band of frequencies $\{\omega_{on}\}$ would be affected if the pulses were evenly spaced with eigenvalues inversely proportional to $\tau_s + \tau_d$, or

$$\omega_{0n} = \frac{2\pi n}{(\tau_s + \tau_d)}. \tag{57}$$

(v) *Noise decoupling*

As pointed out by Ernst [32], noise decoupling introduces a term into the quantum Liouville equation which acts like a relaxation process. Recently McClung and John [33] have considered both planar and spherical noise decoupling in $A_n X_m$ systems. The multipole formulation of noise decoupling takes on a simple form. The multipole basis for $A_n X_m$ systems is taken to be the direct product of two multipole operators for the strongly coupled A system and the strongly coupled X system,

$$|k_A q_A v_A k_X q_X v_X\rangle\rangle = T^{k_A q_A}(v_A) T^{k_X q_X}(v_X) \tag{58}$$

and the quantum Liouville equation is modified to read

$$i\hbar \frac{\partial \phi^{k_A q_A k_X q_X}(v_A v_X)}{\partial t} = \sum_{\substack{k_A' q_A' v_A' \\ k_X' q_X' v_X'}} \langle\langle k_A q_A v_A k_X q_X v_X | \mathscr{L} - K \mathscr{V}\mathscr{V} | k_A' q_A' v_A' k_X' q_X' v_X'\rangle\rangle \phi^{k_A' q_A' k_X' q_X'}(v_A' v_X') \tag{59}$$

$\mathscr{L}$ is the usual Liouville superoperator and $\mathscr{V}$ is the noise coupling operator [32], $\mathscr{V}A = [V, A]_-$. The constant K gives the amplitude of the noise.

For planar decoupling of the X spins the operator $\mathscr{V}\mathscr{V}$ is

$$\mathscr{I}_x^X \mathscr{I}_x^X \equiv I_x^X, [I_x^X, \quad]_-]_- , \tag{60}$$

while for spherical decoupling $\mathscr{V}\mathscr{V}$ is

$$\mathscr{V}\mathscr{V} = \mathscr{I}_x^X \mathscr{I}_x^X + \mathscr{I}_y^X \mathscr{I}_y^X = \mathbf{I}^X \cdot \mathbf{I}^X - \mathscr{I}_z^X \mathscr{I}_z^X . \tag{61}$$

Spherical decoupling is thus diagonal in the multipole basis giving

$$-K\langle\langle k_A q_A v_A k_X q_X v_X | \mathbf{I}^X \cdot \mathbf{I}^X - \mathscr{I}_z^X \mathscr{I}_z^X | k_A' q_A' v_A' k_X' q_X' v_X'\rangle\rangle = -K(k_X(k_X+1) - q_X^2)\, \delta_{k_A k_A'}\, \delta_{q_A q_A'}\, \delta_{v_A v_A'}\, \delta_{k_X k_X'}\, \delta_{q_X q_X'}\, \delta_{v_X v_X'}. \tag{62}$$

This shows that all the multipole basis elements associated with the X spins decay to zero for large K except the non-magnetic operators with $k_X = 0$.

For planar decoupling it is easily shown that the operator

$$\mathscr{I}_x^X \mathscr{I}_x^X = (\mathscr{I}_+^X + \mathscr{I}_-^X)(\mathscr{I}_+^X + \mathscr{I}_-^X) \tag{63}$$

mixes double quantum coherences with the diagonal frequencies. These observations are in agreement with those reported in [32].

6. Discussion

Spin decoupling techniques include a number of pulse sequences [11, 13]. The physical rationalization of these is usually restricted to a vector model while calculations treat the evolution of the density operator as a series of unitary transformations. An example of the former is the composite pulse decoupling of Freeman [11, 29] and of the latter, average hamiltonian theory and its applications [28, 10]. Most treatments ignore the evolution of the spins under their coupling while the pulse is on, and include such effects only between pulses. In this limit, the approach presented here takes on a very simple form by being a product of matrix multiplication for rotations $\mathbf{D}^k(\Omega_i)$ and evolutions $\mathbf{M}^{kk'}(\tau_j)$ for the ith pulse and the jth interval.

For the case of composite pulses, for example, the vector model is extended from the vector magnetization to any polarization with rotationally invariant tensor properties. Hence we expect a composite pulse sequence which compensates its own off-resonance distribution for the *vector* magnetization to have a similar compensating effect on the higher *tensor* polarizations. Moreover, by organizing a pulse sequence into multipoles, it is possible to include higher than the zeroth order term used in average hamiltonian theory [11] to study cyclic pulse sequences.

For several spins, the polarizations of the different spin magnetizations may be simultaneously pulsed. The multipole approach for 2 spins presented here separates the vector magnetizations into $\phi_q^1(10)$ and $\phi_q^1(01)$. For multispin systems this is straightforwardly generalized to the ith spin by calculating $\phi_q^1(0--1--0)$. A simultaneous pulse on two spins, however, will cause rotation of both frequencies of the appropriate bilinear operator coupling the two. Improved understanding of the success of, for example, the INEPT and DEPT sequences and their modifications [13] may result from such considerations. One of the more recent studies of spin decoupling shows the effects of 'illusions' of spin decoupling [28] arising from a difference in magnitude or phase between the $\mathbf{I}_1$ and $\mathbf{I}_2$ scalar coupled spins at the beginning of the decoupling period. The interpretation of these effects lies in the existence of initial multilinear terms. In their analysis of a two spin system, Levitt *et al.* [28] modify the initial spin density matrix from $\sigma(0) = I_{ix}$ to various bilinear operators [17], e.g. $2I_{1x}I_{2z}$. In the treatment presented here, all such initial conditions are simultaneously taken into account. For example, in (36) any initial polarization can be made non-zero and the result calculated by a simple Laplace inverse. One may choose, say, $\phi_1^1(10)[0]\alpha\langle I_{1+}\rangle[0] \neq 0$ and $\phi_0^1(01)[0]\alpha\langle I_{2z}\rangle[0] \neq 0$ with all others zero, or alternately keep $\chi_a^{\pm}(11)[0]\alpha\langle[\mathbf{I}_1\tau_2]_q\rangle[0] \neq 0$ and all others zero. This will permit a systematic quantitative analysis of all possible spin illusions for a scalar coupled pair discussed in reference [28].

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