Multiple-Pulse n.m.r. Experiments in Solids: An Introduction to Symmetrized Pulse Sequences [and Discussion]

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Multiple-pulse n.m.r. experiments in solids: an introduction to symmetrized pulse sequences

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The study of solids by n.m.r. has been greatly facilitated with the development, over the last 10 years or so, of sophisticated r.f. multiple-pulse experiments designed to reduce the dipolar interaction. Often when the intrinsic dipolar line broadening is selectively reduced in many materials, smaller and usually more interesting chemical shift and exchange interactions are revealed that reflect the solid state electronic structure around the resonant nuclei. This situation obtains in liquids, of course; however, in solids the full interaction tensor components are measurable and yield valuable additional information on the chemical bonding.

In this paper the development of the various multiple pulse techniques is reviewed and their detailed operation described in a consistent formalism.

1. INTRODUCTION

The uninitiated practioner of n.m.r. might well be forgiven for thinking that solid materials, being highly ordered phases of matter, should be simpler to study and interpret by standard n.m.r. techniques than liquids. That this is not so is manifest in the growing wealth of applications of high-resolution n.m.r. in liquids and liquid-like systems. It is an interesting paradox that the very nature of the random motions in a liquid, which complicate certain aspects of interpretation, in particular spin lattice relaxation processes, at the same time greatly simplify the high-resolution spectra by virtue of the complete removal of the dipole–dipole interaction and the partial removal of the chemical shift tensor. In solids, of course, the lack of motion of the atoms or molecules allows the dipolar interaction to dominate the absorption spectrum. As a result, the line shapes of powdered crystalline substances and amorphous materials are in general uninteresting. Of course, if the dipolar interaction were somehow removed in a solid, then the expectation of the novice could well be approached, especially at low temperatures, where internal molecular motions could be substantially reduced and even halted, depending on the activation energy of the solid system being studied.

The first approach to the problem of removing dipolar interactions in solids was that of Andrew *et al.* (1958) and Lowe (1959). In these approaches, the solid was rotated at high speed about an axis inclined 54.74° to the static magnetic field vector, the so-called magic axis. Of course, the motion of the molecules in the solid is correlated, unlike that of a liquid, and the dipolar interaction is reduced in this instance by virtue of the rotational transformation dependence of the dipolar interaction strength on the angle between the rotation axis and the static field vector.

Rotation about the magic axis also removes chemical shift anisotropy. In this sense the absorption line shape is more akin to that of a liquid. Unfortunately, sample rotation is not generally applicable to the study of solids since it turns out for homogeneously broadened lines that to achieve the desired line-narrowing one must rotate the specimen at a frequency at least equal to the static dipolar line width. Depending on the nuclear species, this can vary from a few kilohertz for phosphorus compounds to a few tens of kilohertz for fluorinated compounds to perhaps 100 kHz for the broadest proton line shapes. Practical problems limit rotor speeds to around 8 or 9 kHz. Nevertheless, valuable results have been obtained by the method and are discussed in a later paper (Andrew, this symposium).

An alternative approach to the removal of dipolar interactions and indeed other second-rank tensor interactions like the high field quadrupolar interaction has been developed by Waugh *et al.* (1968), Mansfield (1970), Mansfield *et al.* (1973) and Rhim *et al.* (1973), and is based on the manipulation of the dipolar interaction spin operators rather than the spatial and angular coordinates. In those so-called multi-pulse line-narrowing experiments, the solid remains stationary, and if a single crystal, in a preferred orientation with respect to the static field. The spin operators are manipulated by applying short resonant 90° r.f. pulses with various r.f. carrier phase shifts and spacing as described later. In rough analogy with specimen rotation, the pulse repetition frequency has to be greater than the static dipolar line width to achieve significant line narrowing. However, it is readily appreciated that pulse spacings of a few microseconds can easily be achieved with modern pulse spectrometers. Such closely spaced pulses are equivalent to rotation speeds in excess of 100 kHz. Thus, as we shall demonstrate, it is now possible to contemplate multi-pulse line narrowing experiments on a much wider class of materials, including some of the broadest proton resonances.

Following a brief introduction to the basic theory of line narrowing, some recent exciting developments of the subject will be reviewed and some new results presented.

2. Elementary theory

To gain a basic understanding of multi-pulse line narrowing experiments, especially the more esoteric experiments described later on, it seems appropriate to review briefly the fundamental theory.

We therefore start our discussion by considering the transient response or free induction decay (f.i.d.) from a dipolar broadened solid. We shall assume that the system of interacting spins, I, is initially in thermal equilibrium and polarized in a magnetic field $\boldsymbol{B}$ $(0, 0, B_0)$ along the z axis. In the high-temperature approximation, the equilibrium density matrix for the system is given by

$$\rho_0 = \exp(-\hbar H/kT)/\mathrm{tr}(1), \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature and the total system Hamiltonian $H\hbar$ is

$$\hbar H = (H_0 + H_i)\,\hbar, \tag{2}$$

in which H_0 is the Zeeman term given by

$$H_0 = -\omega_0 I_z, \tag{3}$$

where $I_z = \sum_i I_{zi}$ and is the total z component of spin I.

The interaction term H_i comprises the following:

$$H_i = H_\mathrm{d} + H_\mathrm{e} + H_\mathrm{c} + H_\mathrm{o}, \tag{4}$$

where the Van Vleck truncated dipolar interaction term H_d is given by

$$H_\mathrm{d} = \sum_{i<j} A_{ij}(\boldsymbol{I}_i \cdot \boldsymbol{I}_j - 3I_{zi}I_{zj}), \tag{5}$$

the electron coupled exchange interaction is given by

$$H_{\mathrm{e}} = \sum_{i<j} \tilde{A}_{ij} \boldsymbol{I}_i \cdot \boldsymbol{I}_j, \tag{6}$$

and the chemical shift and resonance offset terms H_{c} and H_{o} are given by

$$H_{\mathrm{c}} + H_{\mathrm{o}} = \sum_i (\delta_i + \Delta\omega)\, I_{zi}. \tag{7}$$

All other terms have their usual meanings; tr used in (1) and below denotes the trace or diagonal matrix sum.

For our purposes, in calculating the initial density matrix we may ignore terms H_i and consider only the first spin-dependent part of the expansion of (1) in which we write

$$\rho_0 \approx a I_z, \tag{8}$$

where the constant a is given by $a = \hbar\omega_0/kT \operatorname{tr}(1)$. (8 *a*)

In this expression the Larmor angular frequency, ω_0, is given by

$$\omega_0 = \gamma B_0, \tag{9}$$

where γ is the magnetogyric ratio.

When disturbed from the equilibrium state, the density matrix describing the evolution of the spin system is described by the von Neumann equation of motion

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[H, \rho], \tag{10}$$

with the general solution

$$\rho(t) = \left\{\hat{T} \exp\left(\mathrm{i}\int_0^t H(t')\,\mathrm{d}t'\right)\right\}^{\dagger} \rho(0) \left\{\hat{T} \exp\left(\mathrm{i}\int_0^t H(t')\,\mathrm{d}t'\right)\right\}, \tag{11}$$

where $\rho(0)$ is the density matrix at time $t = 0$. The time-ordering operator $\hat{T}$ is introduced here, since it is not always true that $H(t)$ will commute with itself for different times. We shall return to ordering operators later. For the present, (11) greatly simplifies when the Hamiltonian operator is not time-dependent. In this case we drop the ordering operator and $\rho(t)$ becomes

$$\rho(t) = \mathrm{e}^{-\mathrm{i}Ht} \rho(0)\, \mathrm{e}^{\mathrm{i}Ht}. \tag{12}$$

As we shall see, this equation is central to the development of multi-pulse theory. For introductory texts on the use of the density matrix in n.m.r., see the books by Abragam (1961) and Slichter (1978).

2.1. *Rotating reference frame*

An important simplification of the theory is to perform our calculations in the rotating reference frame, i.e. a frame rotating at or close to the Larmor angular frequency. We apply an r.f. rotating magnetic field $\boldsymbol{B}_1(-B_1 \sin\omega t, \ -B_1 \cos\omega t, 0)$ chosen to rotate in the same sense as the Larmor precession of the spins (actually, a negative Euler rotation about the z axis). If B_1 is large enough, i.e. $\gamma B_1 \gg H_i$, the total Hamiltonian acting during the pulse may to a first approximation be taken as

$$H = -\omega_0 I_z + \omega_1 \mathrm{e}^{\mathrm{i}\omega t} I_y\, \mathrm{e}^{-\mathrm{i}\omega t}, \tag{13}$$

where $\omega_1 = \gamma B_1$. (13 *a*)

When (13) is substituted into (10) and subsequently transformed into the rotating reference frame according to the transformation

$$\rho^*(t) = \mathrm{e}^{\mathrm{i}H_0 t} \rho(t)\, \mathrm{e}^{-\mathrm{i}H_0 t}, \tag{14}$$

we obtain the new von Neumann equation of motion

$$\mathrm{d}\rho^*/\mathrm{d}t = -\mathrm{i}[-\Delta\omega I_z + \omega_1 I_y], \tag{15}$$

where the resonance offset $\Delta\omega = \omega_0 - \omega$.

The solution of (15) when $\Delta\omega = 0$, that is at resonance, is

$$\rho^*(t) = \mathrm{e}^{-\mathrm{i}\omega_1 I_y t}\rho(0)\,\mathrm{e}^{\mathrm{i}\omega_1 I_y t}. \tag{16}$$

We note that $\rho_0^* = \rho_0$ so that if we apply an r.f. pulse of duration t_w to the equilibrium magnetization, i.e. $\rho(0) = \rho_0 = aI_z$, then we can write (16) as

$$\rho(t_\mathrm{w}) = a\mathrm{P}_y^\dagger(\Theta)\, I_z \mathrm{P}_y(\Theta), \tag{17}$$

where now $\mathrm{P}_y(\Theta)$ is a pure rotation operator about the y axis, given in this case by

$$\mathrm{P}_y(\Theta) = \mathrm{e}^{\mathrm{i}\Theta I_y}. \tag{18}$$

At this point, i.e. (17), we drop the asterisk, the rotating frame henceforth being implied. The pulse nutation angle, Θ, is given by

$$\Theta = \gamma B_1 t_\mathrm{w}. \tag{18a}$$

The utility of representing the r.f. pulses by rotation operators will become apparent, especially with complex pulse sequences when $\Theta = 90°$. $\mathrm{P}_y(90)$ has the following properties:

$$\left.\begin{aligned} \mathrm{P}_y^\dagger I_x \mathrm{P}_y &= -I_z; \\ \mathrm{P}_y^\dagger I_y \mathrm{P}_y &= I_y; \\ \mathrm{P}_y^\dagger I_z \mathrm{P}_y &= I_x. \end{aligned}\right\} \tag{19}$$

Similarly for $\mathrm{P}_x(90)$ we obtain

$$\left.\begin{aligned} \mathrm{P}_x I_x \mathrm{P}_x^\dagger &= I_x; \\ \mathrm{P}_x I_y \mathrm{P}_x^\dagger &= -I_z; \\ \mathrm{P}_x I_z \mathrm{P}_x^\dagger &= I_y. \end{aligned}\right\} \tag{20}$$

The dagger, †, used here and previously denotes the Hermitian adjoint. For the r.f. pulses considered, the adjoint amounts to a 180° phase shift of the carrier wave. We shall find it convenient therefore to denote the pulses as $\mathrm{P}_x^\dagger = \mathrm{P}_{-x}$, etc.

2.2. *Single pulse response*

After a single 90° r.f. pulse, the effective Hamiltonian in the rotating frame is just H_i. The normalized transverse response function of the spins, sometimes called the free induction decay (f.i.d.), is calculated from the density matrix by using the following expression:

$$\langle I_x(t)\rangle = \mathrm{tr}\,(\rho(t)\, I_x)/\langle I_x\rangle_0. \tag{21}$$

Thus at time $(t+t_\mathrm{w})$, the f.i.d. following one 90° r.f. pulse is

$$\langle I_x(t+t_\mathrm{w})\rangle = \mathrm{tr}\,(\mathrm{e}^{-\mathrm{i}H_i t}\mathrm{P}_{-y} I_z \mathrm{P}_y \mathrm{e}^{\mathrm{i}H_i t} I_x)/\langle I_x\rangle_0. \tag{22}$$

Equation (22), though seemingly simple, turns out to be a *tour de force* to calculate exactly for systems comprising more than two interacting spins (Lowe & Norberg 1957; Clough & McDonald 1965; Tjon 1966; Evans & Powles 1967). The difficulty arises entirely from the bilinear spin operators occurring in the dipolar interaction.

2.3. *Double pulse response*

If we make B_1 in (18*a*) very large, t_{w} becomes correspondingly smaller for a 90° pulse. In the limit of vanishing t_{w}, the r.f. pulses approach delta functions, a state impossible to realize in practice. However, for most practical purposes, we may ignore t_{w} and take our pulse rotation operators as acting in infinitely short times. We stress, however, that for multi-pulse purposes this turns out to be an invalid assumption, even for $t_{\mathrm{w}} \leqslant 1.0\,\mu\mathrm{s}$, a typical 90° pulse length for solid studies. We shall refer to this later.

If a second r.f. pulse is applied along the x axis at time τ following the first pulse, the response at time $(t+\tau)$ is given by

$$\langle I_x(t+\tau)\rangle = \mathrm{tr}\,(\mathrm{e}^{-\mathrm{i}H_i t}\mathrm{P}_x\,\mathrm{e}^{-\mathrm{i}H_i\tau}\mathrm{P}_{-y}I_z\mathrm{P}_y\,\mathrm{e}^{\mathrm{i}H_i\tau}\mathrm{P}_{-x}\,\mathrm{e}^{\mathrm{i}H_i t}I_x)/\langle I_x\rangle_0. \tag{23}$$

This equation, first evaluated exactly for dipole pairs (Powles & Mansfield 1962), predicts a signal decay followed by a signal growth or solid echo peaking when $t = \tau$ for small values of τ. Evaluation for more than two spins by using a series expansion method predicts that solid echoes occur quite generally (Powles & Strange 1963; Mansfield 1965; see also the review by Mansfield (1972)). The rotation pulses are of course unitary, that is to say

$$\mathrm{P}_y^{\dagger}\mathrm{P}_y = 1, \text{ etc.} \tag{24}$$

By inserting two unitary operators appropriately into (23), the expression may be simplified somewhat by noting that

$$\mathrm{P}_x\,\mathrm{e}^{-\mathrm{i}H_i\tau}\mathrm{P}_x^{\dagger} = \mathrm{e}^{-\mathrm{i}\tilde{H}_i\tau}, \tag{25}$$

where in fact

$$\tilde{H}_i = \mathrm{P}_x H_i \mathrm{P}_x^{\dagger}. \tag{25a}$$

This may be verified by expanding (25) and calculating the effect of P_x term by term. This contraction of the rotation operators may be systematically used in more complex pulse sequences, which we now discuss.

2.4. *Generalized multiple pulse response*

We now consider a series of r.f. pulses applied to the spin system in n repeating groups of m which may in turn comprise m' subgroups. It is convenient to generalize our notation in this case. By a process of repeated contraction as indicated above, the transverse response is given at time t by

$$\langle I_x(t)\rangle = \mathrm{tr}\,(Q^{\dagger n}I_x\,Q^n I_x)/\langle I_x\rangle_0, \tag{26}$$

which may be written more conveniently by introducing a logarithmic operator through the identity

$$Q = \mathrm{e}^{\ln Q} \tag{27}$$

as

$$\langle I_x(t)\rangle = \mathrm{tr}\,(\exp\left[(\ln Q^{\dagger}/\mathrm{i}t_{\mathrm{c}})\,t\right]I_x\exp\left[(\ln Q/\mathrm{i}t_{\mathrm{c}})\,t\right]I_x)/\langle I_x\rangle_0, \tag{28}$$

where Q is the spin propagator operator given by

$$Q = \prod_{\mu=0}^{m}\prod_{\mu'=0}^{m'}\exp\,(\mathrm{i}H_i^{\mu\mu'}a_{\mu\mu'}\tau). \tag{29}$$

The transformation of the interaction Hamiltonian H_i^{00} under the action of successive pulse rotations $\mathrm{P}_{\alpha\alpha'}$ is given by

$$H_i^{\mu\mu'} = \left(\prod_{\alpha=0}^{\mu}\prod_{\alpha'=0}^{\mu'}\mathrm{P}_{\alpha\alpha'}\right)^{\dagger}H_i^{00}\left(\prod_{\alpha=0}^{\mu}\prod_{\alpha'=0}^{\mu'}\mathrm{P}_{\alpha\alpha'}\right). \tag{30}$$

The minimum number of pulses necessary to realize full symmetry of H_i^{00}, i.e. to bring it back to H_i^{00}, constitutes a *cycle* or a *subcycle* (Waugh *et al.* 1968). In this notation the dwell time in a given Hamiltonian state regarded here as being periodically switched through several states, is $a_{\mu\mu'}\tau$, where τ is a convenient minimum unit of time. The cycle time t_c is given by

$$t_c = \sum_0^m \sum_0^{m'} a_{\mu\mu'}\tau = \sum_0^m t_{c_\mu}, \tag{31}$$

where t_{c_μ} is the μth subcycle time.

The initial interaction Hamiltonian state $H_i^{00} = H_i$. We also note that the above formalism assumes an initially perturbed density matrix $aI_x = a\mathrm{P}_y I_z \mathrm{P}_y$. This initial P_y pulse is put on our figures but is not always necessary.

The propagator operator Q is, from (29), just an ordered product of non-commuting exponential operators. It is a simple matter to convince oneself that non-commuting exponential operators may be handled in much the same way as commuting operators provided the result is properly ordered. For example,

$$\mathrm{e}^{A_1}\mathrm{e}^{A_2} \neq \mathrm{e}^{A_1+A_2} \tag{32}$$

$$= \hat{\mathrm{O}}\,\mathrm{e}^{A_1+A_2}, \tag{32a}$$

where in this case the ordering operator $\hat{\mathrm{O}}$ is introduced to make sure that A_1 always precedes A_2 from left to right. This simple result is true for any number of non-commuting operators. We now apply this result to (29) for the operator Q and obtain

$$Q = \hat{\mathrm{O}} \exp \sum_0^m \sum_0^{m'} \mathrm{i} H_i^{\mu\mu'} a_{\mu\mu'}\tau, \tag{33}$$

where $\hat{\mathrm{O}}$ orders the Hamiltonian terms in ascending (or descending) rank in μ and μ'.

Expanding the exponential we obtain the alternative expression

$$Q = 1 + \sum_{l=1}^{\infty} (\mathrm{i}\tau)^l\, V_l^{mm'}/l!, \tag{34}$$

in which

$$V_l^{mm'} = \hat{\mathrm{O}}\left(\sum_0^m \sum_0^{m'} a_{\mu\mu'} H_i^{\mu\mu'}\right)^l. \tag{35}$$

We are now in a position to examine term by term the exponents in the response function, equation (28). The logarithmic operator is given by

$$\begin{aligned}\ln Q = {} & \mathrm{i}\tau V_1^{mm'} + \tfrac{1}{2}(\mathrm{i}\tau)^2\{V_2^{mm'} - (V_1^{mm'})^2\} \\ & + (\tfrac{1}{6})\,(\mathrm{i}\tau)^3\{V_3^{mm'} - (V_1^{mm'})^3 - \tfrac{1}{4}[V_1^{mm'}[V_2^{mm'} - (V_1^{mm'})^2] + [V_2^{mm'} - (V_1^{mm'})^2]\,V_1^{mm'}]\} \\ & + \dots.\end{aligned} \tag{36}$$

It is clear from the definition of (35) that

$$V_1^{mm'} \bigg/ \sum_0^m \sum_0^{m'} a_{\mu\mu'} = \bar{H}_i \tag{37}$$

is just the average interaction Hamiltonian operating over the cycle or subcycle. It is also apparent that the ordering operator plays no role here. However, it definitely cannot be ignored for $l > 1$. Before proceeding to examine these cases, it is perhaps worth pointing out that in terms of line narrowing efficiency, systematic removal of at least the dipolar parts of the first and all

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parts of successive higher order terms in (36) is desirable. That is to say, if possible, we require that

$$(V_1^{mm'})_{\mathrm{d}} = 0, \tag{38a}$$

$$V_2^{mm'} - (V_1^{mm'})^2 = 0, \tag{38b}$$

$$V_3^{mm'} - (V_1^{mm'})^3 = 0, \tag{38c}$$

$$V_4^{mm'} - (V_1^{mm'})^4 = 0, \text{ etc.}, \tag{38d}$$

where the subscript refers to the dipolar contribution only.

2.5. *Ordering and symmetrizing*

To see how we might achieve the required vanishing of at least the second- and third-order terms in (36), we must examine the differences between an ordered and a symmetrized operator product. If these can be made equal for $l = 2$ and 3 we have achieved our aim.

One important and useful fact in the elimination of the unordered terms in (36) is the fact that if $V_1^{mm'}$ vanishes independently over each subgroup m' then we can effectively forget it when considering $V_2^{mm'}$. Equally, if $V_2^{mm'}$ vanishes separately over its subgroup, which may itself be a set of subgroups of V_1, then we can be sure that it will not reintroduce terms when considering $V_3^{mm'}$. Consider an equally spaced three-state subcycle with average Hamiltonian

$$\bar{H}_i = (\tfrac{1}{3})\, V_1^{1,3} = \sum_{\mu'} (\tfrac{1}{3})\, H_i^{1,\mu'}. \tag{39}$$

The dipolar part, $(V_1^{1,3})_{\mathrm{d}}$, may be made to vanish if the three Hamiltonian states are chosen as follows:

$$H_i^{1,\mathrm{X}} = \sum_{i<j} A_{ij}(\boldsymbol{I}_i\cdot\boldsymbol{I}_j - 3I_{xi}I_{xj}) + \sum_i \delta_i I_{xi} + \sum_{i<j} \tilde{A}\boldsymbol{I}_i\cdot\boldsymbol{I}_j; \tag{40a}$$

$$H_i^{1,\mathrm{Y}} = \sum_{i<j} A_{ij}(\boldsymbol{I}_i\cdot\boldsymbol{I}_j - 3I_{yi}I_{yj}) + \sum_i \delta_i I_{yi} + \sum_{i<j} \tilde{A}\boldsymbol{I}_i\cdot\boldsymbol{I}_j; \tag{40b}$$

$$H_i^{1,\mathrm{Z}} = \sum_{i<j} A_{ij}(\boldsymbol{I}_i\cdot\boldsymbol{I}_j - 3I_{zi}I_{zj}) + \sum_i \delta_i I_{zi} + \sum_{i<j} \tilde{A}\boldsymbol{I}_i\cdot\boldsymbol{I}_j; \tag{40c}$$

where for convenience we replace $\mu' = 1, 2, 3$ by X, Y, Z. The average Hamiltonian is then

$$\bar{H}_i = (\tfrac{1}{3}) \sum_i \delta_i (I_{xi} + I_{yi} + I_{zi}) + \sum_{i<j} \tilde{A}_{ij}\boldsymbol{I}_i\cdot\boldsymbol{I}_j. \tag{41}$$

From our earlier statement we may well inquire as to the rules for vanishing $V_1^{mm'}$ and $V_2^{mm'}$ when considering cycles comprising subcycles. To clarify this we take a specific example. Let us consider a cycle comprising two three-state subcycles. In our notation, then

$$V_1^{1,6} = V_1^{1,3} + V_1^{2,3} \tag{42}$$

and

$$\begin{aligned} V_2^{1,6} &= \hat{\mathrm{O}}(H_1^{1,1} + H_1^{1,2} + H_1^{1,3} + H_1^{2,1} + H_1^{2,2} + H_1^{2,3})^2 \\ &= \underset{1\to 2}{\hat{\mathrm{O}}_m}\underset{1\to 3}{\hat{\mathrm{O}}_{m'}}[V_1^{1,3} + V_1^{2,3}]^2 \\ &= \underset{1\to 3}{\hat{\mathrm{O}}_{m'}}[(C_1^{1,3})^2 + 2V_1^{1,3}V_1^{2,3} + (V_1^{2,3})^2] \\ &= V_2^{1,3} + V_2^{2,3} + \hat{\mathrm{O}}_{m'}\, 2V_1^{1,3}V_1^{2,3}. \end{aligned} \tag{43}$$

From above, the second-order term in (36)

$$(V_1^{1,6})^2 - V_2^{1,6} = \underset{1\to 3}{\hat{\mathrm{O}}_{m'}}\, 2V_1^{1,3}V_1^{2,3} - V_1^{1,3}V_1^{2,3} - V_1^{2,3}V_1^{1,3}, \tag{44}$$

and this can be made to vanish identically provided that the ordering operator is replaced by a symmetrized ordering operator $\hat{O}_S$, which forces symmetrical states from the ordered product. This amounts to choosing the states in $V_1^{2,3}$ to be reflexions of the states in $V_1^{1,3}$. This argument is quite general (Mansfield 1970; Wang & Ramshaw 1972).

We next discuss cycles which exploit reflexion symmetry.

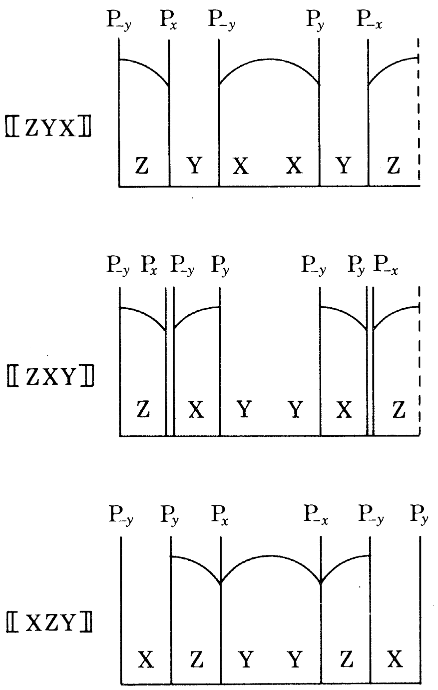

Figure 1. Sketch showing the pulse sequences for three of the six forms of the three-state reflexion symmetry cycle.

2.5.1. *Reflexion symmetry*

As discussed above, and by more general symmetry arguments developed elsewhere (Mansfield 1970, 1971), it has been shown that a cycle comprising all permutation groups of the three Hamiltonian states of (40) will make $V_2^{mm'}$ vanish. However, the vanishing occurs in pairs of subgroups each comprising the above-mentioned three states. Moreover, the second subgroup terms are in reflexion symmetry to the first subgroup. That is to say, if we represent the three Hamiltonian states by the shorthand X, Y or Z, then a reflexion symmetry group is written as XYZZYX and the repeated cycle as $(\text{XYZZYX})^n$, where n is the number of cycles or groups. In this notation, the WAHUHA cycle (Waugh *et al.* 1968), the first to remove successfully the dipolar interaction by using a non-symmetrized combination of Hamiltonian states, is written as $(\text{XXYXXY})^n$. However, it is readily seen that when repeated, a reflexion symmetry cycle with shifted origin is obtained. Naturally, if this were the only difference one could say unequivocally that the WAHUHA and reflexion symmetry cycles were equivalent. But as we shall see when considering real cycles subject to the imperfections of the spectrometer, symmetry is important for practical compensation schemes.

2.5.2. *Notation*

I have already introduced some shorthand notation for cycles when written out explicitly in terms of the equally weighted switched Hamiltonian states by using parentheses ( ). That is to say,

$$\begin{aligned}(\mathrm{XYZZYX}) &= (\mathrm{XYZ})\,(\mathrm{ZYX}) \\ &= \llbracket \mathrm{XYZ} \rrbracket,\end{aligned}$$

where I now introduce the open brackets denoting reflexion symmetry of the states. It will also be convenient to describe several reflexion symmetry cycles, in which case I shall write

$$\begin{aligned}\llbracket \mathrm{XYZ} \rrbracket \llbracket \mathrm{XYZ} \rrbracket &= \llbracket \mathrm{XYZ;\ XYZ} \rrbracket \\ &= (\mathrm{XYZ})\,\llbracket \mathrm{ZYX} \rrbracket\,(\mathrm{ZYX}).\end{aligned}$$

Notice that this notation is really a shorthand way of representing a cycle by the first-order average Hamiltonian extant over the cycle. Since the first-order Hamiltonian is linear in spin operators over the cycle (or subcycle), we can allow for situations when, with suitable pulses, a linear Z state, i.e. $\delta_i I_{zi}$ is inverted to $-\delta_i I_{zi}$. Our shorthand for this case is $\bar{\mathrm{Z}}$, etc. Of course, the bilinear dipolar Hamiltonian terms are always positive, and in any case are removed in first order.

With compound cycles including negative states, it will later be convenient to introduce the idea of cycle contraction. For example, the sequence

$$\llbracket \mathrm{XYZ;\ X\bar{Y}Z} \rrbracket = \{\mathrm{XZ}\}$$

where the single braces denote a single contraction of a double three-state reflexion symmetry cycle. An obvious extension of the same notation leads to a doubly contracted cycle, namely

$$\llbracket \mathrm{XYZ;\ X\bar{Y}\bar{Z}} \rrbracket = \{\!|\mathrm{X}|\!\}, \text{ etc.,}$$

where the open brace denotes a double contraction of a double three-state reflexion symmetry cycle.

3. PULSE SEQUENCES

Starting with our basic building block, the three-state subcycle (XYZ), it is clear that we can build six different reflexion symmetry cycles. These are

$$\llbracket \mathrm{XYZ} \rrbracket,\ \llbracket \mathrm{ZXY} \rrbracket,\ \llbracket \mathrm{YZX} \rrbracket,$$

$$\llbracket \mathrm{XZY} \rrbracket,\ \llbracket \mathrm{ZYX} \rrbracket,\ \llbracket \mathrm{YXZ} \rrbracket.$$

Actual pulse sequences necessary to achieve three of these cycles are shown in figure 1.

Examination of $V_3^{mm'}$ shows that only the dipolar part, $(V_3^{mm'})_{\mathrm{d}}$, can be made to vanish over three reflexion symmetry subcycles comprising all the permutation symmetry states of XYZ. For example the cycle

$$\llbracket \mathrm{ZXY;\ XZY;\ ZYX} \rrbracket$$

is represented as a pulse sequence in figure 2.

The sequences referred to work only for idealized 90° r.f. pulses in which $t_{\mathrm{W}} \to 0$. In actual pulse sequences t_{W} cannot be ignored and this has led to various modifications of the basic sequences above to compensate for two major pulse imperfections.

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3.1. *Compensated cycles*

Two major imperfections of the simple four-pulse cycles discussed above which vitiate their performance in practice are the finite pulse width, typically 1.0 μs, and the r.f. inhomogeneity. The latter effect introduces a distribution of nutation angles around the desired 90° condition, which can deviate by several degrees.

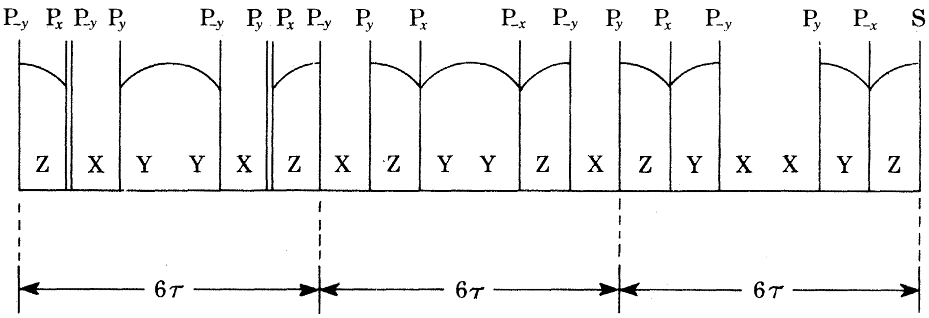

FIGURE 2. Sketch showing the pulse sequence for one form of an *uncompensated* fully permuted symmetry cycle, $[\![ZXY; XZY; ZYX]\!]$. S denotes the sampling pulse.

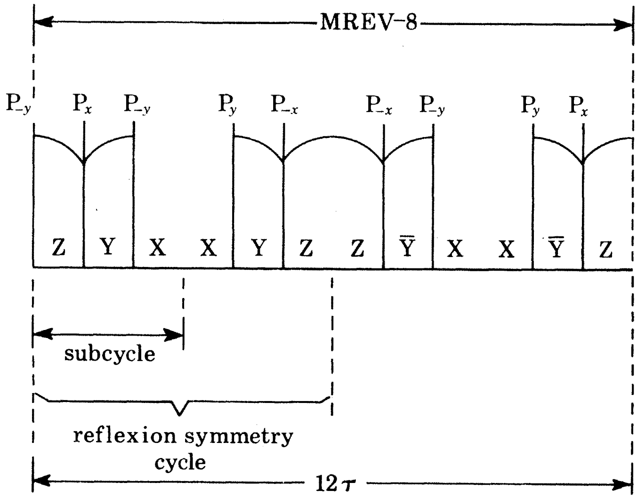

FIGURE 3. Sketch of the compensated reflexion symmetry or MREV-8 cycle, $[\![ZYX; Z\bar{Y}X]\!]$. Compensation is for finite pulse width and r.f. inhomogeneity.

Fortunately both of these effects can be removed in one modification, first shown theoretically by Mansfield (1970, 1971) and later verified experimentally by Mansfield *et al.* (1973) and also by Rhim *et al.* (1973). The procedure is to follow one reflexion symmetry cycle by a second in which the r.f. carrier phases of, say, the x pulses *only* are reversed. Such a cycle is shown in figure 3. Since it involves eight-pulses this cycle is referred to by some authors (Haeberlen 1976; Mehring 1976) as the MREV-8 cycle, after its inventor and some of its practitioners.

In the notation adopted here, the MREV-8 cycle is denoted as

$$[\![ZYX; Z\bar{Y}X]\!].$$

Of course, all six versions of the basic reflexion symmetry cycle may be so compensated, but in compensating in this manner, the new cycle is actually asymmetric. The detailed theory

(Mansfield 1971) shows that second-order terms may actually be reintroduced unless $[V_1^{1,6}, V_1^{2,6}] = 0$, where $V_1^{1,6}$ refers to the first half of the MREV-8 cycle and is represented in shorthand by ZYX, while $V_1^{2,6}$ refers to the second half-cycle represented by $\mathrm{Z\bar{Y}X}$. In practice this may be simply overcome by symmetrizing the whole cycle, i.e. by adding a further cycle to give

$$[\![\mathrm{ZYX};\ \mathrm{Z\bar{Y}X}]\!]\,[\![\mathrm{Z\bar{Y}X};\ \mathrm{ZYX}]\!].$$

Such cycles have been compared experimentally with their asymmetric forms and found to give indistinguishable line-narrowing performance (Garroway *et al.* 1975). This result suggests that although some symmetrization is important, complete symmetry may not be necessary. Mansfield (1971) had suggested using compensated MREV-8 cycles as better building blocks with which to achieve full permutation symmetry cycles. There are several approaches that one can take to achieve this. In Mansfield's original approach, the MREV-8 cycles were designed in such a manner that each one had the same scaling factor. However, before elaborating on this, we briefly discuss what we mean by scaling factors.

3.2. *Scaling factors*

In the three-state subcycle (XYZ), the average Hamiltonian is

$$\bar{H}_i = (\tfrac{1}{3}) \sum_i \delta_i (I_{xi} + I_{yi} + I_{zi}). \tag{45}$$

In the rotating reference frame, this represents a rotation about the cubic body diagonal. If such a transformation is performed, $\bar{H}_i$ in this frame becomes

$$\begin{aligned} \bar{H}_i &= 3^{-\frac{1}{2}} \sum_i \delta_i I_{z'_i} + \sum_{i<j} \tilde{A}_{ij} \boldsymbol{I}_i \cdot \boldsymbol{I}_j \\ &= S \sum_i \delta_i I_{z'_i} + \sum_{i<j} \tilde{A}_{ij} \boldsymbol{I}_i \cdot \boldsymbol{I}_j, \end{aligned} \tag{46}$$

where the scaling factor $S = 3^{-\frac{1}{2}}$ and effectively *reduces* the chemical shift interaction and offset term if present by this amount. For the idealized WAHUHA and uncompensated $[\![\mathrm{ZYX}]\!]$ cycles the scaling factors are all $S = 3^{-\frac{1}{2}}$. The scaling factors are slightly modified by the non-zero r.f. pulse length, and detailed expressions are given elsewhere (Mansfield 1971; Mansfield *et al.* 1973; Garroway *et al.* 1975). For simplicity in this account I shall deal exclusively with the ideal scaling factors.

For compensated cycles like MREV-8, we notice that the appearance of a negative linear Hamiltonian state means that the average Hamiltonian is reduced from three states to an effective average Hamiltonian with only two states, i.e., in the contraction bracket notation,

$$[\![\mathrm{ZYX};\ \mathrm{Z\bar{Y}X}]\!] = \{\mathrm{ZX}\},$$

with an average Hamiltonian

$$\bar{H}_i = (\tfrac{1}{3}) \sum_i \delta_i (I_{zi} + I_{xi}) + \sum_{i<j} \tilde{A}_{ij} \boldsymbol{I}_i \cdot \boldsymbol{I}_j. \tag{47}$$

The chemical shift and/or resonance offset term in (47) represents a rotation about a cube face diagonal and gives a scaling factor $S = \frac{1}{3}\sqrt{2}$. (N.B.: in the papers of Garroway *et al.* (1975) and Morris *et al.* (1979), the scaling factors, in their notation f, have been defined as the inverse of the definition adopted here, i.e. $S = 1/f$.)

3.3. *Permuted symmetry cycles*

As discussed earlier, permuted symmetry cycles may also be constructed from their corresponding compensated MREV-8 cycles. However, this may be done in several ways. The first way that we shall consider is one that preserves the scaling factor over each subcycle (Mansfield 1971). For example, the fully permuted cycle

$$[\![\mathrm{ZYX};\, \mathrm{Z\bar{Y}X}]\!]\,[\![\mathrm{XZY};\, \mathrm{XZ\bar{Y}}]\!]\,[\![\mathrm{ZXY};\, \mathrm{ZX\bar{Y}}]\!] = \{\mathrm{ZX}\}\{\mathrm{XZ}\}\{\mathrm{ZX}\}$$

would have an ideal scaling factor of $\frac{1}{3}\sqrt{2}$. The contracted sequence notation loses the cyclic permutation information, but retains the average Hamiltonian information. I shall refer to this sequence as a fully permuted type 1 or FP_1-n cycle, where n is the number of r.f. pulses required to generate a single cycle. The above cycle may be symmetrized overall, i.e.

$$\{\mathrm{ZX};\ \mathrm{XZ};\ \mathrm{ZX}\}\{\mathrm{ZX};\ \mathrm{XZ};\ \mathrm{ZX}\},$$

where the semicolon introduced here represents two braces, }{. Alternatively we may symmetrize over each sub-MREV-8 cycle, thus:

$$\{\mathrm{ZX};\ \mathrm{ZX}\}\{\mathrm{XZ};\mathrm{XZ}\}\{\mathrm{ZX};\mathrm{ZX}\}.$$

However, as stated previously, this resymmetrization does not seem to make too much difference in practice. In any event, the scaling factor remains unchanged.

Another way of permuting MREV-8 cycles, first suggested and demonstrated by Garroway *et al.* (1975), purposely does *not* preserve the scaling factor over each MREV-8 subcycle. The reason for doing this is basically experimental, namely that to generate the above FP_1-n sequence requires additional r.f. pulses, which in general vitiate the performance of the sequence unless very special care is taken to compensate the cycle further. Thus, for example, if in each subcycle contraction we make a *different* state vanish, we get a second fully permuted cycle that I shall denote as a type 2 or FP_2-n cycle; for example,

$$[\![\mathrm{ZYX};\mathrm{Z\bar{Y}X}]\!]\,[\![\mathrm{ZXY};\mathrm{Z\bar{X}Y}]\!]\,[\![\mathrm{YXZ};\mathrm{YX\bar{Z}}]\!] = \{\mathrm{ZX}\}\{\mathrm{ZY}\}\{\mathrm{YX}\}.$$

This cycle has full permutation symmetry even in the contracted form. However, it does not have individual MREV-8 symmetry. It will be obvious to the reader that in the new notation there are six equivalent versions of this FP_2 cycle.

3.3.1. *Partly permuted cycles*

A cycle comprising two MREV-8 cycles only, i.e. {ZX}{ZY}, was proposed and tried by Garroway *et al.* (1975) and subsequently used in ^{19}F chemical shift studies in some liquid crystals (Jasinski *et al.* 1976, 1978; Morris *et al.* 1979). Since the chosen Hamiltonian states join nicely between cycles, only eight pulses for each MREV-8 cycle are required, the whole cycle requiring 16 r.f. pulses and lasting a period of 12τ. This is therefore referred to as a PP_2-16 cycle since it is a contracted cycle of the second kind. Figure 4 shows the actual pulse sequence used to generate this cycle. The ideal scaling factor is $S = 6^{-\frac{1}{2}}$. The advantage of this cycle over the MREV-8 cycle is that $(V_3^{1,24})_{\mathrm{d}}$ is reduced to half the value in the eight-pulse cycle, i.e. $(V_3^{1,24})_{\mathrm{d}} = \frac{1}{2}(V_3^{1,12})_{\mathrm{d}}$. This gives a much improved resolution, especially close to resonance.

3.3.2. *Fully permuted cycles*

One difficulty with FP_2-n cycles, for example

$$\{\mathrm{ZX}\}\{\mathrm{ZY}\}\{\mathrm{YX}\},$$

is that in the third subcycle, the Hamiltonian has to switch from a Z state to a Y state at the third subcycle boundary. This can be achieved by using two extra 90° pulses, making an FP_2-26 cycle. This cycle has been tried experimentally (Morris 1977), but showed no great improvement over the PP_2-16 cycle. However, part of its apparent failure to improve resolution can no doubt be ascribed to r.f. pulse imperfections, including phase glitch errors, which could have been corrected for (Mansfield & Haeberlen 1973). Recently, however, Burum & Rhim (1979) have proposed a modification, which, although apparently breaking the subcyclic symmetry, achieves

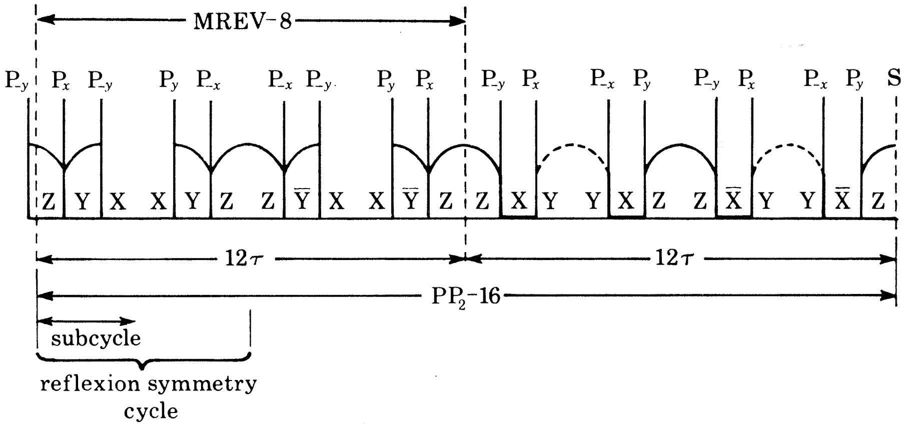

FIGURE 4. Two different MREV-8 cycles joined to give a partly permuted (PP_2-16) cycle of the second kind (see text for details). Notice that the whole sequence is built up of three-state subcycles that make the first-order dipolar Hamiltonian vanish. S is the sampling pulse. (Garroway *et al.* (1975); Morris *et al.* (1979).)

the required Hamiltonian states *without* the extra two pulses referred to above. However, as we have already noted, subcycle symmetry of mixed bilinear and linear Hamiltonian terms does not exist anyway, so one might expect that asymmetric rearrangements of the Hamiltonian states would not be too important. Their modified FP_2-24 cycle is denoted as follows:

$$\{ZX\}[\![ZXY]\!](ZXY)\{YX\}(Y\bar{X}Z),$$

which derives simply from

$$\{ZX\}\{ZY\}\{YX\}$$

by writing out in full the central $\{ZY\}$ cycle and transposing the subcycle and group $(Y\bar{X}Z)\{YX\}$ by $\{YX\}(Y\bar{X}Z)$. This now ensures that the overall cycle automatically starts and finishes in a Z state and avoids the extra two pulses referred to above. This exchange of subgroups does not matter, of course, in $V_1^{1,24}$. It clearly makes no difference, for the dipolar parts of $(V_2^{1,24})_d = 0$ or $(V_2^{1,6})_d = (V_2^{2,6})_d = (V_2^{3,6})_d = 0$. Also, by inspection, $(V_3^{1,24})_d = 0$, since it is a fully permuted symmetry cycle. The only worry is whether non-zero cross-terms are reintroduced into $V_2^{1,24}$. If they are, they can be removed by overall reflexion symmetry. However, as we shall see, the experimental evidence is that there is little or no difference between the FP_2-24 sequence and the symmetrized FP_2-52 version. For further details I refer the reader to the paper of Burum & Rhim (1979). The ideal scaling factor for all FP_2-n cycles is $S = \frac{2}{9}\sqrt{3}$ (Morris 1977). Other valid versions of the FP_2-n cycle can be derived from the six FP_2 cycle states, e.g.

$$\{ZX\}\{ZY\}\{YX\} \rightarrow \{ZX\}[\![ZXY]\!](Z\bar{X}Y)\{YX\}(Y\bar{X}Z);$$
$$\{YX\}\{YZ\}\{ZX\} \rightarrow \{YX\}[\![YXZ]\!](Y\bar{X}Z)\{ZX\}(Z\bar{X}Y);$$
$$\{XZ\}\{XY\}\{YZ\} \rightarrow \{XZ\}[\![XZY]\!](X\bar{Z}Y)\{YZ\}(Y\bar{Z}X).$$

Notice that all the modified cycles start and end in the *same* Hamiltonian state. Yet other viable cycles may be obtained from the above three by cyclic and/or permutation changes, *mutatis mutandis*, by using the initial subcycles {YZ} or {ZY} or {XY}. However, some combinations may well require more than 24 r.f. pulses to produce, thus making them less attractive to generate. In all cases, the cycle period $t_c = 36\tau$.

Finally we note that doubly contracted cycles of the type

$$\{|\mathrm{X}|\}\{|\mathrm{Y}|\}\{|\mathrm{Z}|\} = \{|\mathrm{X};\mathrm{Y};\mathrm{Z}|\}$$

and

$$\{|\mathrm{X}|\}\{|\mathrm{X}|\}\{|\mathrm{X}|\} = \{|\mathrm{X};\mathrm{X};\mathrm{X}|\}$$

may also be produced and are a kind of logical inverse of the previously discussed singly contracted cycles. The scaling factor for the $\{|\mathrm{X};\mathrm{Y};\mathrm{Z}|\}$ cycles is $S = 3^{-\frac{1}{2}}$, which actually represents an improvement in scaling. For the $\{|\mathrm{X};\mathrm{X};\mathrm{X}|\}$ cycle the scaling factor $S = \frac{1}{3}$.

The $\{|\mathrm{X};\mathrm{Y};\mathrm{Z}|\}$ cycle, like the WAHUHA cycle in first order, corresponds in the rotating reference frame to a rotation of the transverse magnetization about a cubic body diagonal. To be consistent with the previous notation, I refer to these doubly contracted sequences as fully permuted cycles of the 1 d and 2 d kind, namely,

$$\mathrm{FP}_{1\mathrm{d}}-n \equiv \{|\mathrm{X};\mathrm{X};\mathrm{X}|\} = \{|\mathrm{Y};\mathrm{Y};\mathrm{Y}|\};$$

the Z type does not exist since evolution of magnetization is invariant to straightforward rotation about the z axis. Also

$$\begin{aligned}\mathrm{FP}_{2\mathrm{d}}-n \equiv \{|\mathrm{X};\mathrm{Y};\mathrm{Z}|\} &= \{|\mathrm{Y};\mathrm{Z};\mathrm{X}|\} = \{|\mathrm{Z};\mathrm{X};\mathrm{Y}|\}\\ &= \{|\mathrm{X};\mathrm{Z};\mathrm{Y}|\} = \{|\mathrm{Y};\mathrm{X};\mathrm{Z}|\} = \{|\mathrm{Z};\mathrm{Y};\mathrm{X}|\}.\end{aligned}$$

As with the singly contracted cycles, the $\mathrm{FP}_{2\mathrm{d}}$ cycles can be rearranged to start and finish in the same Hamiltonian state, for example

$$\{|\mathrm{Z};\mathrm{X};\mathrm{Y}|\} = \{|\mathrm{Z}|\}\,(\mathrm{ZXY})\,\{|\mathrm{Y}|\}\,\llbracket\bar{\mathrm{Z}}\mathrm{X}\bar{\mathrm{Y}}\rrbracket\,(\mathrm{YXZ}),$$

or better still

$$\{|\mathrm{Z};\mathrm{X};\mathrm{Y}|\}\{|\mathrm{Y};\mathrm{X};\mathrm{Z}|\},$$

this latter sequence having a cycle time, $t_c = 72\tau$. I point out that a subcycle of the type $\{|\mathrm{X}|\}$ is generated with the pulse sequence

$$P_{-y}[\tau P_x \tau P_{-y} 2\tau P_y \tau P_x 2\tau P_x \tau P_{-y} 2\tau P_y \tau P_x \tau]^n.$$

This simple cycle appears to be fully compensated for r.f. inhomogeneity and finite pulse width, but the other forms may not be. Whether the gains in generating properly compensated versions of these new cycles warrant the effort is a matter for experiment and remains to be seen. My feeling is that an increased scaling factor, together with full permutation symmetry, bodes well for a genuine improvement of resolution of the order of $\frac{3}{2}$ over that currently obtainable with FP_2-24 cycles.

4. EXPERIMENTAL RESULTS

The first true line narrowing sequence to yield chemical shift information was the four-pulse WAHUHA cycle (Waugh *et al.* 1968). This sequence has produced a wealth of valuable information on the chemical shift tensor and exchange interactions in solids. It is probably the easiest sequence to use and therefore still finds wide application, particularly for ^{19}F resonances where the chemical shifts are relatively large.

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The improved MREV-8 cycle has found growing application in the study of ^{1}H resonances in solids (Haeberlen 1979, and this symposium). A phase-compensated version of this sequence (Mansfield & Haeberlen 1973) makes this cycle quite stable and relatively easy to set up.

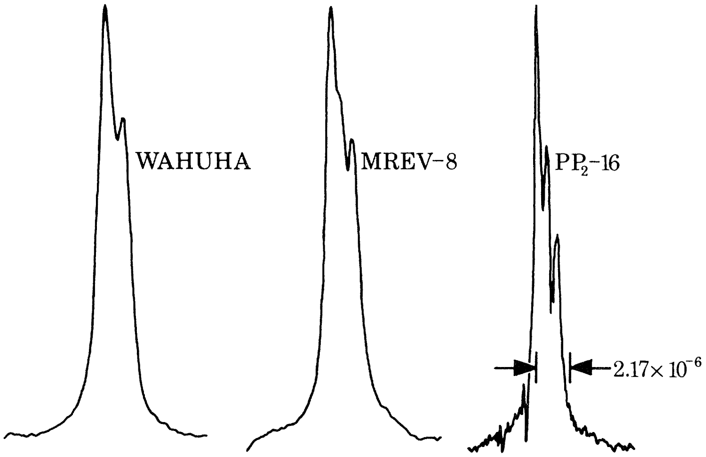

FIGURE 5. Comparison of the resolution from three different line-narrowing pulse sequences on the proton resonance in a single crystal of calcium formate. The crystal was rotated about the *c* axis and just resolves three of the four non-equivalent proton sites (B_0 approximately midway between the *a* and *b* axes). The minimum pulse spacing τ was 4.0 μs and t_w = 1.0 μs for all cycles. All measurements were made at 200 MHz. (See acknowledgment.)

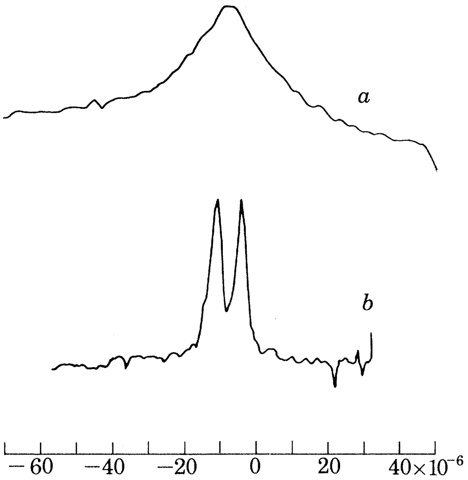

FIGURE 6. Experimental comparison of the resolution of the MREV-8 and FP$_2$-52 pulse sequences on a single crystal of gypsum. Curve *a* is the line shape from the MREV-8 sequence and *b* that obtained from an FP$_2$-52 sequence. In both cases τ = 2.8 μs and t_w = 1.5 μs. Result taken from Burum & Rhim (1979).

The PP$_2$-16 sequence has so far found little application, even though in its phase-uncompensated form it is found to be quite stable and relatively easy to align. Its superior line-narrowing ability, particularly for small resonance offsets, has been demonstrated by Garroway *et al.* (1975) on ^{19}F in a single crystal of CaF$_2$ with B_0 along the [111] axis. However, a more convincing test of the relative merits of all three cycles has been done on the ^{1}H resonance of a single crystal of a Ca(COOH)$_2$ rotated about the *c* axis with B_0 approximately between the *a* and *b* axes. In this orientation there are three resolved lines arising from the four chemically inequivalent proton sites. The results are shown in figure 5. The degree to which the lines are resolved gives a good comparative indication of the efficacy of the pulse sequence used. The experiments were performed at 200 MHz on a Bruker CXP-200 pulse spectrometer in collaboration with Dr H. Post of Bruker A.G., Karlsruhe, Germany. An important point in this comparative study is that the pulse alignment, performed initially on water, was not altered for any of the sequences tested.

A striking comparison between the line narrowing ability of an MREV-8 and an FP_2-52 pulse sequence has recently been demonstrated by Burum & Rhim (1979) on the hydrate protons in a single crystal of gypsum ($Ca_2SO_4 . 2H_2O$). Their result is reproduced in figure 6 and shows a chemical shift between inequivalent protons of about 10×10^{-6}, which is completely masked by residual dipolar broadening in the MREV-8 cycle. This result is most gratifying to see since it is the first experimental demonstration that full permutation symmetry cycles are worth using.

Chemical shift anisotropy of protons in ice has also been demonstrated with the use of the same sequence. The authors also state that there is virtually no difference in the line narrowing ability of the FP_2-52 and FP_2-24 sequences.

5. CONCLUSIONS

During the last decade or so, steadily developing multiple-pulse techniques, though creating a wide interest, have generally not stimulated the response from physical chemists that one might have initially supposed. Part of the problem is the complexity of the sequences and rather special electronic expertise required to make them work. The now available commercial pulse spectrometers remove this daunting obstacle and on this basis alone one might expect to see the subject flourish in the next few years.

New experiments have now demonstrated conclusively that the more sophisticated cycles employing partial or full permutation symmetry of the Hamiltonian states during a cycle are really worth pursuing. The most recent striking results on ^1H in gypsum and particularly ice, which is one of the broadest dipolar line widths normally encountered in n.m.r. studies in solids, show that a much wider class of compound can now be profitably studied in the solid state. It is to be hoped that these results will encourage others to take up the standard in the pursuit of yet higher resolution. A few new cycles for them to try out are suggested in this paper. Meanwhile, the currently attainable line-narrowing efficiency opens up new and exciting applications for multi-pulse studies in solids. Central among these is the continued study of chemical shift tensors and exchange interactions. Other possibilities include the suppression of quadrupole interactions, for example in metals and metal alloys, the suppression of the dipolar interaction in spin dynamical experiments and finally the possibility of using these line narrowing sequences for n.m.r. imaging in solids (Mansfield & Grannell 1975).

The author is grateful to Dr H. Post and Mr B. Knüttel of Bruker A.G., Karlsruhe, for their help in using the CXP-200 spectrometer to obtain the results in figure 5, and their kind hospitality during my brief visit.

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Discussion

J. G. Powles (*The Physics Laboratories, The University of Kent, Canterbury, U.K.*). The apparent necessity of using 24, or more, ideally infinitesimally short, radio-frequency pulses with as small a spacing as possible to remove dipolar broadening in solids while leaving other more interesting interactions, suggests to me that the matter has got out of hand and that evolutionary development is in danger of producing a dinosaur. It seems to me that at this stage one ought to consider going back to *one* pulse of finite length. This single pulse would be a complex entity but in principle no less complex than the present group of pulses. The requirements for this single pulse are immediately obtained by Fourier transformation, e.g. finite pulse lengths in the original pulses transforming to finite frequency range in the single pulse, etc. There may well be advantages in addition to the technical one of having to generate only a single, albeit complex, pulse. Rather than attempting to produce the desired elimination of the dipolar interaction by successively removing error terms in powers of the pulse spacing, one would presumably attempt to approach the ideal by progressive increase in accuracy in the morphology of the single pulse. This could well be a more profitable procedure since it could correspond, by analogy with perturbation theory, to a partial infinite summation rather than successive approximation in a power series which is notoriously inefficient beyond the first few terms.

P. Mansfield. Professor Powles has made a number of interesting observations on which I should like to comment in turn. The approach outlined in my paper has led to a systematic way of reducing the multi-pulse line width by exploiting the symmetrization of the switched dipolar Hamiltonian substates. The expected improvements in resolution seem to be realizable in practice. A reduction in the number and complexity of the pulses would be welcome, but I suspect that things would become more rather than less complex by adopting an analytical approach via the frequency domain. The reason behind this is based on the spin behaviour of some earlier and simpler multi-pulse experiments. The response to a train of equally spaced 90° r.f. pulses (no r.f. carrier phase shifts) was found experimentally to have a very slight oscillation of the first few solid echo amplitudes (P. Mansfield & D. R. Ware, *Phys. Rev.* **168**, 318 (1968)). This eventually settled to what appeared to be a monotonic exponential decay of successive echo peaks.

It was clear that the iteration procedures then used to predict the long-time signal behaviour, based on projection of the short-time behaviour, could not explain this oscillatory effect.

The initial behaviour was subsequently understood by Fourier analysing the r.f. pulse train into its zeroth and higher frequency components, and, as a first approximation, considering the response of the spin-locked magnetization in the zeroth frequency r.f. component only. In this case the signal was found to oscillate about a slightly decaying baseline corresponding to a cross-polarization between the spin dipolar energy reservoir and the effective Zeeman energy reservoir in the rotating frame. For long times ($T_2 < t \ll T_1$), the spin system settled to a final thermodynamic equilibrium magnetization.

Efforts to improve the description of the long-time behaviour in these simple experiments have led others (see, for example, L. N. Erofeev *et al.*, *Proc. chem. Soc. Faraday Symp.* no. 13, p. 1 (1978)) to extend the thermodynamic approach to include more Fourier components of the pulse sequence.

If r.f. carrier phase shifts are introduced, as with the most efficient line narrowing cycles, it is not clear whether a thermodynamic approach would still be valid.

With Professor Powles's last point concerning partial infinite sums, it is perhaps worth pointing out that since the logarithm of the spin propagator operator is truncated in the exponent of the spin evolution matrix, it is equivalent to an infinite order time perturbation approximation and not a truncation of a power series to the first few terms. That is why, of course, the description of multiple-pulse experiments is exact in the first order (V_1).