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COMPOSITE PULSES

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"So you say you want a revolution"—Lennon/McCartney

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1. INTRODUCTION

An enormous body of radio-frequency (r.f.) pulse sequences has been developed in recent years for the purpose of 'spin manipulations'. Examples include excitation of single-quantum and multiple-quantum coherences,[1,2] inversion and equalization of spin populations,[3,4] and transfer of

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information from one coherence to another.[5–8] Sequences have also been devised for changing the effective Hamiltonians under which the spin system evolves, as in homonuclear[9,10] and heteronuclear[11–23] decoupling experiments. Despite the universal use of pulse excitation in modern Fourier transform NMR, until recently the r.f. pulse itself had not been subject to much criticism and the following question had not often been asked: is there in fact a better, or a more versatile way to manipulate the spin system than by isolated r.f. pulses of constant amplitude and phase?

It is clear that the standard rectangular r.f. pulse may be considered a special case of a general irradiation strategy in which both amplitude and phase (or equivalently frequency) are made arbitrarily time-dependent. It is likely that in the future a better understanding of modulated pulses will lead to the adoption of irradiation schemes quite different from the rectangular pulse familiar today. The technology for the generation of r.f. pulses with continuously modulated amplitude and phase is starting to become available and shapes with highly intriguing properties have been suggested.[24–31] However in this article we will concentrate on a class of less general modulation schemes which at the moment are easier to implement and to analyze than the continuous cases. Instead of one pulse, simply a series of rectangular pulses of possibly different durations and phases is applied. Such 'composite pulses'[32–50] are usually designed to perform an equivalent transformation of the spin system as an ideal single pulse. However in many cases composite pulses may remedy some of the defects of the conventional single pulse by being less sensitive to the precise value of the r.f. field, and less demanding on peak power. In addition composite pulses may be designed with characteristics quite different from ordinary pulses, for example the ability to perform rotations about the *z*-axis of the rotating frame,[35,41] or to operate selectively within a narrow band of r.f. field strengths.[43,46,47]

Perhaps the first recognizable composite pulses are the so-called '2–1–4' sequences of Redfield.[51] These sequences were designed to improve the frequency selectivity of a single rectangular r.f. pulse. Consider a single weak pulse applied at the frequency of some desired resonance, for example from a solute spin system in low concentration. By careful adjustment of pulse power and duration, it is possible to arrange that a signal resonating at a slightly different frequency, for example from the solvent, is left unexcited. For a single pulse the adjustment is highly critical and in the case of a spatially inhomogeneous r.f. field, the 'nulling' of the solvent resonance is impossible to achieve completely. Redfield recognized that a suitable series of pulses could behave better in this respect; the null could be made broader and less dependent on r.f. field strength. Recently these 'solvent suppression' sequences have been developed further. The one which is now generally agreed to behave most satisfactorily is the '1–3–3–1' sequence discovered independently by Turner[52] and Hore.[53,54] Hore's article[54] is referred to as a detailed treatment of solvent suppression sequences. We will not refer to them again, except to note that at least in the initial stages of their treatments, all of these workers employed a linear approximation of the spin response which allows the dependence of excitation on offset from resonance to be estimated by the Fourier transform of the pulse sequence. They were successful because this is not a bad approximation for only small perturbations of the system. The same applies to the 'DANTE' sequence for selective excitation by a chain of short, evenly-spaced pulses developed by Morris *et al.*.[55] Again it can be shown that for small perturbation, the true frequency response corresponds rather closely to the Fourier transform of the excitation.

Linear response theory becomes less useful as a basis for design of a pulse sequence once large perturbations of the spin system are performed. The true frequency response of a 90° pulse, as calculated from the Bloch equations, still resembles the Fourier transform of the excitation quite closely, but strong deviations are already observed for 180° pulses.[30] For flip angles of more than 180° the linear response of the system bears little resemblance to the true behaviour. In cases like heteronuclear decoupling, where many complete rotations are applied, use of Fourier arguments is completely false. Indeed decoupling sequences based on fallacious spectral arguments are now being superseded by composite pulse cycles which use an accurate calculation of the spin evolution well outside the linear regime.[11–23]

For spin systems in isotropic liquids, where spin–spin couplings are small, it is relatively easy to determine the response far outside the linear regime. If relaxation is neglected, the effect of the r.f. pulse is to rotate the magnetization vector (or generally, the spin density operator) about some axis in the rotating frame dependent on the r.f. field strength, the offset of the carrier frequency from resonance, and the phase of the r.f. field. The precise dependencies are well-known and will be given below. The important point here is that the spin system experiences a rotation in a three-dimensional space, which is usually relatively easy to visualize without the help of the linear approximation. It becomes possible to start putting several rotations together in carefully-chosen combinations to cancel out each other's deviations from ideality, a possibility suggested by the use of error-compensation schemes in multiple-spin echo[56] and multiple-pulse homonuclear decoupling experiments.[10]

At first sight however, it does seem unlikely that a small number of pulses can be made to cancel each other's imperfections. With hindsight, it may be made to seem more probable by noting that since rotations form a group, any given rotation can be produced by an infinite number of possible combinations of other rotations. Amongst this multitude of ways of doing exactly the same thing, it is likely that there are some which behave better than a single rotation if each is subject to the same non-idealities. For example, the single rotation 180_0 and the composite rotation $90_{90}180_0 90_{90}$ are equivalent if all rotations are ideal. (The notation is used in which β_ϕ denotes a rotation though an angle β about an axis in the xy-plane, at an angle ϕ from the x-axis.) It may be shown[34] that if all rotation angles are slightly increased in the same proportion, then the composite sequence remains equal to a rotation through 180° about an axis in the xy plane, which is the really important characteristic of a 180° pulse. In contrast the single rotation no longer has this behaviour. In this case the deviation could be produced by an inhomogeneous r.f. field.

It is interesting to reflect that self-compensation of errors in rotation angles may only occur in the regime of non-linear response (large flip angles). In a linear system, in which response is proportional to excitation, two pulses can only be worse than one.

The possibility of self-compensation in the non-linear regime is illustrated more graphically in Fig. 1, which shows a numerical simulation of the effects of the three rotations $(90-\delta)_{90}$

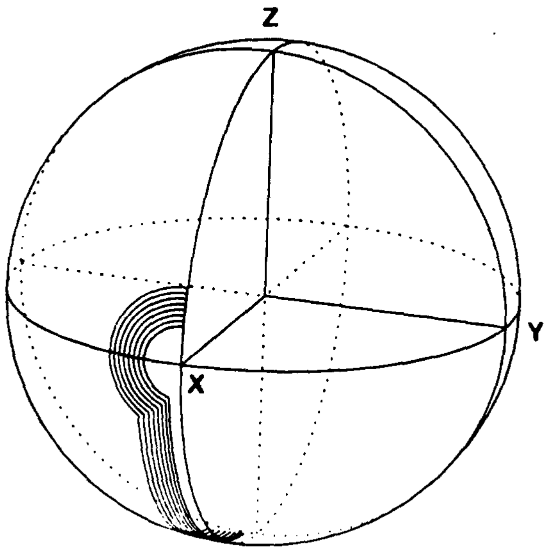

FIG. 1. Tracks traced out on a unit sphere by a family of vectors undergoing the rotations $(90-\delta)_{90}(180-2\delta)_0(90-\delta)_{90}$, where δ varies between 9° and 18°, such as might be produced by the sequence $90_{90}180_0 90_{90}$ in an inhomogeneous r.f. field. The vectors attain final positions much closer to the $-z$-axis than they would have done after a single $(180-2\delta)_0$ rotation. Hence the sequence $90_{90}180_0 90_{90}$ provides an NMR population inversion compensated for r.f. inhomogeneity.

$(180-2\delta)_0(90-\delta)_{90}$ on a family of vectors experiencing a range of r.f. fields.[32] It is clear that when $\delta=0$, the central rotation does nothing and the vector passes cleanly from the z-axis to the $-z$-axis, corresponding to NMR population inversion. The self-compensatory properties of the three rotations are revealed by following the trajectories for small δ. The first rotation takes all vectors in the zx plane from the z-axis towards the x-axis. The vectors land short of the x-axis, however, because of the deviations δ. The next rotation is about the x-axis through the angle $180°-2\delta$. Were this rotation exactly 180°, all vectors would be brought into mirror image positions with respect to the xy plane, and then the final rotation $(90-\delta)_{90}$ would take them all exactly to the $-z$-axis with all non-idealities δ compensated. Of course the central rotation is also actually non-ideal, but the effect of the discrepancy is not too large if δ is small, as is evident in Fig. 1. This is because at the end of the first rotation the vectors are near the x-axis anyway, so the deviation in the 180° rotation can only make its presence felt on the small component which is perpendicular to that axis. This is a higher-order effect. The result is that the family of vectors tend to cluster at the $-z$-axis, and that the pulse sequence $90_{90}180_0 90_{90}$ provides a population inversion rather insensitive to small deviations in the rotation angles.

In Fig. 2 it is shown that the same sequence also provides some compensation if the non-idealities produce instead a 'tilt' in the rotation axes towards the z-axis. This is the case if the pulses are applied off-resonance. The simulated magnetization vectors correspond to resonance offsets in the range $0.4<\Omega/\omega_1^0<0.6$, where Ω is the resonance offset and ω_1^0 the r.f. field strength. Off-resonance effects cause an increase in the rotation angles as well as a tilt of the rotation axis, which is also taken into account in Fig. 2. The effect of the three tilted rotations is less easy to visualize than in Fig. 1, but it is apparent that for this range of Ω/ω_1^0, the vectors also 'bunch' at the $-z$-axis. Hence the sequence $90_{90}180_0 90_{90}$ also provides a 'broadband' population inversion, i.e. a population inversion less sensitive to resonance offsets than that produced by a single pulse. In fact the population inversion is reasonably accurate for all offsets in the range $-1.0<\Omega/\omega_1^0<1.0$.

More recently, much effort has been put into elucidation of the principles of such compensation and for producing more general and more effective composite pulses, suitable for arbitrary manipulations of the spin system in the presence of more general non-idealities and starting from

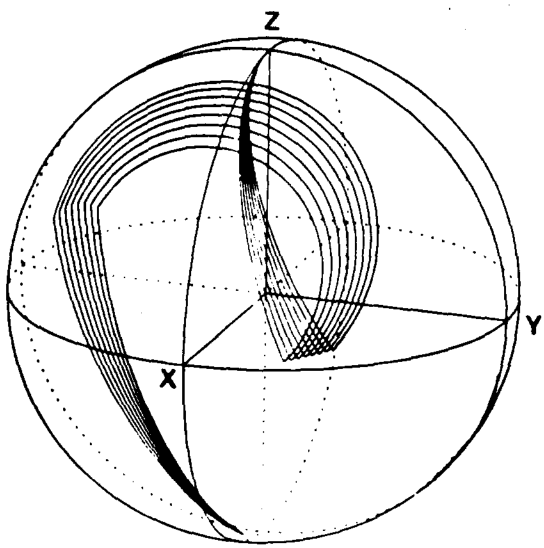

FIG. 2. Tracks traced out on a unit sphere by a family of vectors undergoing a sequence of rotations about tilted axes, such as produced by the sequence $90_{90}180_0 90_{90}$ in the presence of off-resonance effects in the range $0.4<\Omega/\omega_1^0<0.6$. The population inversion is again much more ideal than it would be after a single 180_0 pulse.

more general initial conditions. Much progress has been made, but not all problems have yet been solved. The problem of designing a composite pulse which implements a constant net rotation of any initial condition under arbitrary pulse imperfections has not yet been solved using an acceptably low number of pulses. Were this not the case, the task of writing this review would have been much simpler. As it is, compromise solutions must usually be found according to the degree of knowledge of the initial condition of the spin system, the tolerance of the pulse sequence to particular types of deviations of the rotations from ideality, and the predominant pulse imperfections which are known to exist.

Emphasis will be given to the theoretical aspects of composite pulses, although some practical tips will also be given. This is only in part due to the personal interest of the author. The fact is that composite pulses have not yet been widely used for the application for which they were first intended, error compensation of general pulse experiments in high-resolution NMR. So far the widest use has been in techniques which, though of importance, are essentially 'spin-offs' like broadband heteronuclear decoupling. One can identify many reasons for this. In the first place, commercially available spectrometers have been, and to some extent still are, poorly equipped to handle composite pulses. Accurate r.f. phases are vital for the proper operation of composite pulses, yet in the past most instruments used a method of generating phases by routeing signals through separate pathways having different propagation times, invariably leading to problems of phase inaccuracies and amplitude imbalance. Another important factor blocking the use of composite pulses has been unsatisfactory pulse programming facitilities, making it inconvenient or impossible to implement complicated multiple-pulse sequences. Both of these technological problems are at last showing signs of being recognized and dealt with by the manufacturers. Digital phase shifters have been introduced,[57,58] in which the carrier follows a unique signal path, allowing phase errors or amplitude imbalances to be eliminated, and somewhat more versatile pulse programming hardware and software is more usually available.

However, technological difficulties are not the only reasons why so far composite pulses have not been much used. There are conceptual difficulties. Compensation schemes have often not been based upon unified principles, requiring careful analysis in order to compensate a given pulse sequence. It is not usually possible to 'throw' composite pulses into a pulse sequence and expect them to work. Only recently has it become possible to design procedures with a high degree of generality, as will be shown below. Thus one of the main motivations for this article is to gather together the various theoretical approaches for design of composite pulses and to show the relationship between them. Sometimes the desire to concentrate on the main principles and to present a unified picture has caused the omission of some interesting and perhaps useful composite pulses which in retrospect seem to have a mainly 'historical' significance. I have also readily changed the phases or reversed the order of some of the composite pulses which have already been published when this allows them to be fitted more readily into some conceptual framework. Experimental results are shown only for cases where the outcome may be in doubt; I have not shown experimental verifications of the more trivial transformation properties of composite pulses, which can be found in the original literature. For convenience, I have taken the illustrations from my own work, many of the results shown here having being produced specifically for this article.

The organization of the subject matter is as follows: In Section 2 the basic theory of single r.f. pulses is given briefly, mainly for the sake of establishing notation and concepts for the following Sections. In Section 3 the major theoretical approaches for the design of self-compensating pulse sequences in the high-resolution NMR of isotropic liquids are presented. The discussion may be found rather mathematical for many readers, who may like to skip this Section. In Section 4 the various composite pulse sequences are reviewed, not this time in terms of their principles of construction but more in view of their properties and limitations. A classification of composite pulses on the basis of the type of rotations they produce will be suggested. The classifications A, B1, B2 and B3 for different sorts of composite pulse will be introduced and used to explain under which conditions composite pulses may be inserted into a given pulse sequence. In this Section, different sequences are also compared by means of numerical simulation. In Section 5 some practical applications of error compensation in high-resolution NMR are discussed. In Section 6 a few practical hints as to how composite pulses can be implemented are briefly given. In Section 7 some recent 'unorthodox' applications of composite pulses are touched upon, including the use of rotations about the z-axis, the possibility of achieving spatial selectivity by exploiting r.f. field variations, and the compensation of sequences for variations in coupling constants. In Section 8 the special problems of composite pulses in anisotropic systems are presented. Some closing remarks are given in Section 9.

2. THEORY OF SINGLE PULSES

2.1. *Pulse Propagators*; *Conventions*

In most of this article we discuss the case of NMR in isotropic liquids, where spin–spin couplings are weak and it is easy to dominate them by applying an r.f. field. The subject of composite pulses in solids or anisotropic liquids, where spin–spin couplings are often the principal source of pulse imperfections, is dealt with separately in Section 8.

Considering for simplicity a homonuclear system of spins I_k, the rotating-frame Hamiltonian in the absence of r.f. irradiation may be written

$$H_0 = \sum_k \Omega_k I_{kz} + \sum_{jk} 2\pi J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k, \tag{1}$$

and in the presence of an r.f. field of phase ϕ_p and frequency ω by

$$\begin{aligned} H_p &= H_0 + H_{\mathrm{rf}} \\ H_{\mathrm{rf}} &= \omega_1 \textstyle\sum_k \mathbf{I}_k \cdot \mathbf{n}_{\phi_p} \end{aligned} \tag{2}$$

where

$$\mathbf{I}_k = I_{kx}\mathbf{e}_x + I_{ky}\mathbf{e}_y + I_{kz}\mathbf{e}_z$$

and

$$\mathbf{n}_{\phi_p} = \mathbf{e}_x \cos\phi_p + \mathbf{e}_y \sin\phi_p. \tag{3}$$

Here Ω_k is the resonance offset of spin I_k, defined $\Omega_k = \omega_{0k} - \omega$, where ω_{0k} is the Larmor frequency of spin I_k, J_{jk} are spin–spin couplings, ω_1 is the nutation frequency around the rotating-frame r.f. field, and $\mathbf{e}_x$,$\mathbf{e}_y$ and $\mathbf{e}_z$ are unit vectors along the rotating-frame x,y, or z-axes.

The density operator σ of the spin system evolves during the pulse according to the Liouville–von Neumann equation, neglecting relaxation

$$\dot{\sigma} = -i[H_p, \sigma]. \tag{4}$$

If the pulse is exactly rectangular, meaning the r.f. field rises from zero to its full value instantaneously at the beginning of the pulse and decays to zero instantaneously at the end, and its phase is constant throughout, then H_p is time-independent, and eqn. (4) can be integrated over the duration τ_p of the pulse:

$$\sigma(t + \tau_p) = U_p \sigma(t)\, U_p^{\dagger}, \tag{5}$$

where

$$U_p = \exp(-iH_p\tau_p)$$

and

$$U_p^{\dagger} = \exp(+iH_p\tau_p). \tag{6}$$

The operator U_p is called the pulse *propagator*, and describes the effect of the pulse on arbitrary initial conditions $\sigma(t)$ through eqn. (5). If a sequence of pulses is applied, for example three pulses of durations τ_1, τ_2, τ_3, and possibly different phases or r.f. amplitudes, the overall evolution of the density operator may be evaluated stepwise

$$\sigma(t + \tau_1 + \tau_2 + \tau_3) = U_{123}\sigma(t)\, U_{123}^{\dagger} \tag{7}$$

where

$$U_{123} = U_3 U_2 U_1. \tag{8}$$

The properties of a pulse or sequence of pulses may be discussed either in terms of the transformations it produces of particular initial conditions [eqn. (5)], or in terms of its propagator U [eqn. (6)] which contains the information as to how the pulse transforms all possible initial conditions. In this review, but in contrast with many previous papers, the propagator is considered to act from the *left*, in order to bring the treatment into line with literature in other fields. It should be remembered therefore that chronological order runs in pulse sequences from left to right, but in their propagators from right to left.

It is convenient to mention at this place some other conventions. Firstly, we assume throughout that all frequencies such as Ω_k, ω_1, etc. are positive, unless stated otherwise. With this convention, successive ideal 90_0 rotations take a vector through the positions $z \rightarrow -y \rightarrow -z \rightarrow y$ etc. Secondly, concerning the sign of offset terms Ω_k, we hold to the convention that positive offsets Ω_k are associated with resonances on the right-hand side of the carrier in a conventionally presented spectrum with quadrature detection. This is in fact true for nuclei of positive gyromagnetic ratio. (Nevertheless the behaviour of a pulse sequence at a particular offset will only conform to that predicted if the sense of rotation of the r.f. phases is correctly assigned. A way of checking this latter point is to take a spectrum using a single 90_0 pulse and phase-correct it to pure positive absorption. Then take a spectrum with a 90_{90} pulse and apply the same phase correction. The lines should appear in pure dispersion with the *negative tail on the right*. If the negative tail is on the left, this indicates an incorrect sense of rotation of the phase.)

Further nomenclature concerns the notation for pulse sequences. It is probably impossible to produce a notation which is usable in all contexts. We denote pulses here by $(\beta_p^0)_{\phi_p}$, where β_p^0 indicates the pulse duration τ_p in units of the inverse of the prevailing ('nominal') r.f. field strength ω_1^0 in the sample,

$$\beta_p{}^0 = \omega_1{}^0 \tau_p, \tag{9}$$

and ϕ_p is the r.f. phase. β_p^0 is often referred to as the 'nominal flip angle', a useful but occasionally misleading term, since it really refers to a pulse duration rather than an angle. Both β_p^0 and ϕ_p will usually be given in degrees in this article. When radians are used, they will be given in units of π. The subscripts $x, y, -x$, etc. are only useful for the four orthogonal phases and will be avoided. If the context demands that a pulse is specifically ideal, this will be indicated by a further superscript ^{0}, thus 90_0^0 represents an ideal 90° pulse of phase $\phi_p = 0$.

Subscripts are used for different purposes. Normally it is clear from the context what a subscript means. We will usually keep to the convention that subscripts $k, k' \ldots$ index the spins $I_k, I_{k'} \ldots$ and numerical subscripts or $p, q, l, m, n \ldots$ index the individual pulse elements in a composite pulse. If both are used, the pulse index comes first. A missing spin index usually indicates a sum over all spins, for example $I_z = \sum_k I_{kz}$. Further notation is that $\mathbf{n}$ is a unit vector, and $\mathbf{n}_\phi$ is a unit vector in the xy plane at an angle ϕ from the x-axis.

2.2. *Ideal Pulses*

The ideal pulse is

(a) perfectly rectangular, as mentioned above

(b) employs a perfectly homogeneous r.f. field ($\omega_1 = \omega_1^0$), which

(c) is intense enough that the interaction of the spins with the r.f. field dominates spin–spin couplings and rotating-frame residual longitudinal fields arising from resonance offset effects.

If these conditions are satisfied, terms other than H_{rf} may be ignored during the pulse, and the ideal propagator for a pulse of phase ϕ_p and duration τ_p is given by

$$U_p^0 = \Pi_k \exp\{-i\beta_p^0 \mathbf{I}_k \cdot \mathbf{n}_{\phi_p}\}. \tag{10}$$

The nominal flip angle given by eqn. (9) may be adjusted by changing either the r.f. field strength ω_1^0 or the pulse duration τ_p. The propagator given by eqn. (10) may be interpreted as a 'cascade'[58] of identical, commuting rotations of all spins in the system about the axis $\mathbf{n}_{\phi_p}$ given by eqn. (3).

The transformations induced by such rotations and their application in high-resolution NMR experiments are familiar. Typical transformations induced by ideal 90° pulses include:

(a) conversion of longitudinal into transverse magnetization, e.g.

$$I_{kz} \xrightarrow{90^0_0} -I_{ky} \tag{11}$$

(b) coherence transfer processes, as expressed in terms of Cartesian product operators[60] by such transformations as

$$\begin{aligned} 2I_{kz}I_{k'y} &\xrightarrow{90^0_0} -2I_{ky}I_{k'z} \\ 2I_{kz}I_{k'x} &\xrightarrow{90^0_0} -2I_{ky}I_{k'x} \end{aligned} \tag{12}$$

or in terms of single element product operators[61,62] by transformations like

$$\begin{aligned} I_k^+I_k^\alpha \xrightarrow{90^0_0} \tfrac{1}{4}\{&I_k^+I_{k'}^\alpha + I_k^+I_{k'}^\beta + iI_k^+I_{k'}^+ - iI_k^+I_{k'}^- \\ &+ I_k^-I_{k'}^\alpha + I_k^-I_{k'}^\beta + iI_k^-I_{k'}^+ - iI_k^-I_{k'}^- \\ &+ iI_k^\alpha I_{k'}^\alpha + iI_k^\alpha I_{k'}^\beta - I_k^\alpha I_{k'}^+ - I_k^\alpha I_{k'}^- \\ &- iI_k^\beta I_{k'}^\alpha - iI_k^\beta I_{k'}^\beta + I_k^\beta I_{k'}^+ - I_k^\beta I_{k'}^-\} \end{aligned} \tag{13}$$

Typical transformations induced by 180° pulses include

(a) inversion of longitudinal magnetization

$$I_{kz} \xrightarrow{180^0_0} -I_{kz}, \tag{14}$$

(b) phase reversal of transverse magnetization

$$\mathbf{I}_k\cdot\mathbf{n}_\phi \xrightarrow{180^0_0} \mathbf{I}_k\cdot\mathbf{n}_{-\phi}, \tag{15}$$

(c) interchange of spin states $|m_k\rangle$ with $|-m_k\rangle$, e.g. for a system of two spins-1/2, in terms of single element product operators,[61,62]

$$I_k^+I_{k'}^\alpha \xrightarrow{180^0_0} I_k^-I_{k'}^\beta. \tag{16}$$

Pulses with flip angle of other than 90° or 180° are also often employed. For example, pulses of small flip angle $\beta^0 \ll 1$ radian are frequently used to transfer phase information from a given coherence $|r\rangle\langle s|$ specifically to connected coherences $|r\rangle\langle s'|$ and $|s'\rangle\langle r|$, where $|r\rangle$, $|s\rangle$, $|r'\rangle$ and $|s'\rangle$ are eigenstates of the whole spin system.[5,6] Also 45° pulses are useful in converting longitudinal 2-spin order to observable single-quantum terms[63,64]

$$2I_{kz}I_{k'z} \xrightarrow{45^0_0} \tfrac{1}{2}(2I_{kz}I_{k'z} - 2I_{ky}I_{k'z} - 2I_{kz}I_{k'y} + 2I_{ky}I_{k'y}) \tag{17}$$

2.3. *Non-Ideal Pulses*

In practice, instrumental limitations often prevent the conditions mentioned in Section 2.2 from being met, causing the pulse propagator to deviate from its ideal value, eqn. (10).

(i) *R.f. inhomogeneity.* The type of imperfection which is easiest to analyze arises because the r.f. field inevitably varies from place to place throughout the sample volume. The spatial variation of r.f. fields produced by various coils has been examined theoretically[65] and may be determined experimentally using a version of two-dimensional spectroscopy.[6,66] If the true r.f. field at a given place is ω_1 rather than the nominal value ω_1^0, but is still large enough that H_{rf} dominates H_0 in eqn. (2), then all spins still experience rotations about the same axis $\mathbf{n}_{\phi_p}$, but through a spatially dependent angle $\beta_p = \beta_p^0 \omega_1/\omega_1^0$, rather than through the nominal flip angle β_p^0. R.f. inhomogeneity effects are often small in normal high-resolution NMR systems, but are of increasing importance in large-sample studies and NMR imaging.

The deviation of r.f. field ω_1 from the nominal value ω_1^0 is usually quantified by the parameter $\delta\omega_1/\omega_1^0$, where $\delta\omega_1 = \omega_1 - \omega_1^0$.

(ii) *Phase errors.* It is also possible that the true phase ϕ_p of the r.f. pulse differs from the intended phase because of instrumental defects. However, recent technical improvements such as the introduction of digital phase shifters[57,58] have eradicated this as a long-term problem so phase errors will not be further considered in this work. Accordingly one should be aware that unless very accurate r.f. phases are known to be available, the recommendations of this article could be inappropriate. In fact many composite pulses may be viewed as converting accurate r.f. phases (i.e. accurate rotations around the z-axis) into accurate rotations around other axes such as x or y.

(iii) *Pulse shape errors.* All of the above equations assumed a perfectly rectangular pulse where the r.f. field rises instantaneously from zero at the beginning of the pulse and decays instantaneously at the end, and keeps constant phase throughout. In practice, transients are inevitably encountered at the beginning and end of each pulse which originate from the finite frequency bandwidth of transmitter and probe. They are manifested as a rounding of the pulse shape and phase disturbances during the rising and falling edges.[67] For normal circuits the transients have duration about 1 μsec, and can often be ignored if a 90° pulse has duration around 10μsec or more. The effects are troublesome in solid-state NMR where shorter pulses must often be created. In liquids, where the spread of resonance frequencies is usually smaller, longer pulses can be tolerated where the effect of transients is small. For most of the rest of this paper phase and amplitude transients are therefore ignored. It is therefore advisable never to use more pulse power than is necessary to perform the experiment. This recommendation is valid whether or not composite pulses are used.

(iv) *Off-resonance effects.* If H_{rf} does not greatly exceed H_0, the simultaneous influence of these two non-commuting terms must be taken into account. If internal spin–spin couplings may be ignored during the pulse (which is usually the case), the propagator still factors into a cascade of commuting rotations on all spins I_k in the system, but the rotations on each spin are no longer identical and occur about tilted axes $\mathbf{n}_{p,k}$ not in the equatorial plane of the rotating frame, $\mathbf{n}_{p,k}\cdot\mathbf{e}_z \neq 0$. Also the rotation angles $\beta_{p,k}$ are larger than the nominal flip angle β^0.

Taking into account both off-resonance and r.f. inhomogeneity effects, the propagator for a pulse of phase ϕ_p and nominal flip angle β_p^0 is given by

$$U_p = \Pi_k \exp\{-i\beta_{p,k}\mathbf{I}_k\cdot\mathbf{n}_{p,k}\} \tag{18}$$

with

$$\beta_{p,k} = (\omega_1/\omega_1^0)\beta_p^0[1+(\Omega_k/\omega_1)^2]^{1/2}$$

$$\mathbf{n}_{p,k} = \mathbf{e}_z\cos\theta_k + \mathbf{e}_x\sin\theta_k\cos\phi_p + \mathbf{e}_y\sin\theta_k\sin\phi_p$$

and

$$\tan\theta_k = \omega_1/\Omega_k. \tag{19}$$

The rotation on each spin I_k is determined by the rotation angle $\beta_{p,k}$ and the polar angles θ_k and ϕ_p of the rotation axis. Here θ_k is defined as the declination of the rotation axis from the z-axis, so that $\theta_k = 90°$ for an ideal pulse. This definition is also at variance with many previous publications. but follows the usual definition of polar angles in mathematics.

In solids and liquid crystals, the major source of off-resonance effects for spin 1/2 nuclei arises from dipolar interactions rather than chemical shift terms. Treatment of these systems will be deferred until Section 8.

The implications of the imperfect propagator eqn. (18) may easily be worked out for specific experimental cases using Cartesian product operators.[60] It is often convenient to work with the alternative form of the imperfect propagator given by

$$U_p = \Pi_k \exp\{-i\phi_p I_{kz}\}\exp\{-i\theta_k I_{ky}\}\exp\{-i\beta_{p,k} I_{kz}\}\exp\{i\theta_k I_{ky}\}\exp\{i\phi_p I_{kz}\}. \tag{20}$$

the following transformations have been derived for initial conditions $\sigma(0) = I_{kz}, I_{kx}, I_{ky}$ (omitting the pulse index p for brevity):[60]

$$\begin{aligned}
I_{kz} \xrightarrow{\beta_\phi} & I_{kz}[\cos\beta_k \sin^2\theta_k + \cos^2\theta_k] \\
&+ I_{kx}[\sin\beta_k \sin\phi \sin\theta_k + \sin^2(\beta_k/2)\cos\phi \sin 2\theta_k] \\
&+ I_{ky}[-\sin\beta_k \cos\phi \sin\theta_k + \sin^2(\beta_k/2)\sin\phi \sin 2\theta_k] \\
I_{kx} \xrightarrow{\beta_\phi} & I_{kz}[\sin^2(\beta_k/2)\cos\phi \sin 2\theta_k - \sin\beta_k \sin\phi \sin\theta_k] \\
&+ I_{kx}[\cos\beta_k(\sin^2\phi + \cos^2\phi \cos^2\theta_k) + \cos^2\phi \sin^2\theta_k] \\
&+ I_{ky}[\sin^2(\beta_k/2)\sin 2\phi \sin^2\phi_k - \sin\beta_k \cos\theta_k] \\
I_{ky} \xrightarrow{\beta_\phi} & I_{kz}[\sin^2(\beta_k/2)\sin\phi \sin 2\theta_k + \sin\beta_k \cos\phi \sin\theta_k] \\
&+ I_{kx}[\sin^2(\beta_k/2)\sin 2\phi \sin^2\theta_k - \sin\beta_k \cos\theta_k] \\
&+ I_{ky}[\cos\beta_k(\cos^2\phi + \sin^2\phi \cos^2\theta_k) + \sin^2\phi \sin^2\theta_k].
\end{aligned} \tag{21}$$

Transformations of multiple-spin terms such as $2I_{kz}I_{k'y}$, etc. or individual coherence terms such as $I_k^+ I_k^\alpha$, etc., are easily calculated by taking suitable combinations of the above expressions.

Some of these transformations are of particular importance. For example, it is well-known that a 90° pulse is rather insensitive to off-resonance effects if judged by its ability to transform z-magnetization into the xy plane.[68] Assuming no r.f. inhomogeneity, $\omega_1 = \omega_1^0$, the transformation of I_{kz} is given by

$$I_{kz} \xrightarrow{90_0} I_{kz} n_{kz}^+ + (I_{kx}\cos\phi_k^+ + I_{ky}\sin\phi_k^+)(1-(n_{kz}^+)^2)^{1/2} \tag{22}$$

where the residual longitudinal magnetization n_{kz}^+ is

$$n_{kz}^+ \approx (1-\pi/4)(\Omega_k/\omega_1^0)^2 \tag{23}$$

evaluated to second order in offset Ω_k/ω_1^0. The phase of the transverse magnetization is given to third order in offset by

$$\phi_k^+ \simeq -\pi/2 + \Omega_k/\omega_1^0. \tag{24}$$

Thus the phase error generated by a single pulse is linearly dependent on offset to a very good approximation, and the residual longitudinal magnetization has only a weak quadratic dependence.

The sensitivity of the population inversion induced by a 180° pulse to off-resonance effects is stronger:

$$I_{kz} \xrightarrow{180_0} \simeq I_{kz}(-1 + 2(\Omega_k/\omega_1^0)^2) + \ldots \tag{25}$$

Indeed if the pulse is applied off-resonance, a nominal flip angle β_p^0 cannot be found for which population inversion is ideal.

The performance of 90° and 180° pulses with respect to simultaneous r.f. inhomogeneity and off-resonance effects will be analyzed in more detail in Section 4.

3. THEORY OF COMPOSITE PULSES

3.1. *Geometrical Approach*

Historically the first approach used in designing composite pulses outside the linear regime was by following the trajectory of magnetization vectors starting from some given initial condition, usually $\sigma(0)=I_z$, and observing visually or by geometric construction how the trajectories may be combined in such a way as to cause error compensation.

The composite pulse $90_{90}180_0 90_{90}$ which provides a compensated population inversion, was the first to be constructed in this way[32] and its geometrical interpretation has already been discussed in the introduction. It is fair to say that by virtue of its brevity and simplicity this prototype composite pulse remains one of the most useful. We will meet it again in various guises.

Further applications of the geometric approach, usually with the assistance of computer simulation, produced a stream of composite pulses with different properties over the next few years. We will discuss some of these suggestions later on according to their application. However it is convenient to mention here two examples of composite pulses compensated for r.f. inhomogeneity, because they reveal principles which are interesting in a more general sense.

(i) The composite pulse $90_{90}90_0$ was shown to destroy longitudinal magnetization more efficiently than a single 90° pulse in the case of an inhomogeneous r.f. field and negligible resonance offset.[33] The reason is very simple and is shown in the computer simulation of Fig. 3. The first 90° pulse leaves small longitudinal components of magnetization if the r.f. field is homogeneous. These small residual components are rotated nearly into the xy plane by the second 90° pulse, whilst the desired x-magnetization commutes with the second rotation and is unaffected. In the absence of off-resonance effects, the residual z-magnetization is easily evaluated to second-order in $\delta\omega_1/\omega_1^0$:

$$\langle I_z\rangle^+ \simeq (\pi\delta\omega_1/2\omega_1^0)^2. \tag{26}$$

The quadratic dependence is often referred to as *first order* compensation.

(ii) The composite pulse $90_{180}180_{300}$ was shown to destroy longitudinal magnetization in an inhomogeneous, on-resonance r.f. field more effectively still than the previous pulse.[36] This

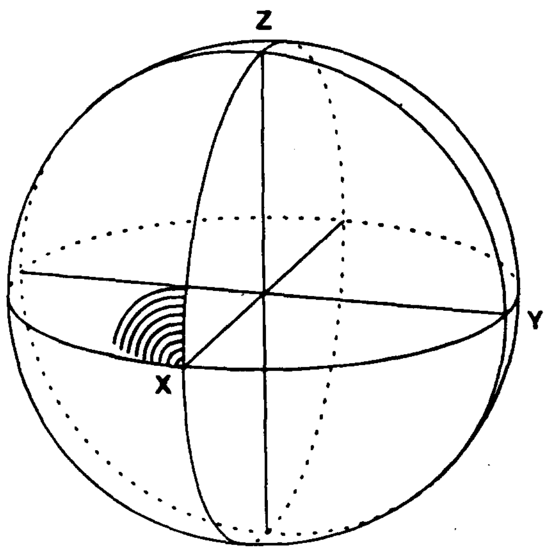

FIG. 3. Tracks traced out by a family of vectors experiencing on-resonance r.f. fields in the range $0.8 < \omega_1/\omega_1^0 <$ 1.0 during the sequence $90_{90}90_0$. The destruction of z-magnetization is compensated for r.f. inhomogeneity.

sequence was constructed by a geometrical argument in which the form of the ideal trajectories at the end of the first pulse and the beginning of the second was examined. Compensation of r.f. inhomogeneity occurs if the ideal trajectories are 'anti-tangential', meaning that at the junction of the two pulses, the magnetization vector exactly reverses its sense of rotation, and if also the arc lengths of the two trajectories are equal. These conditions may be given a more mathematical flavour by the requirement:[36]

$$[\beta_1^0 \mathbf{I}\cdot\mathbf{n}_1^0, \sigma(\tau_1)^0] - [\beta_2^0 \mathbf{I}\cdot\mathbf{n}_2^0, \sigma(\tau_1)^0] = 0 \tag{27}$$

where $\sigma(\tau_1)^0$ is the ideal density operator at the junction of the two pulses:

$$\sigma(\tau_1)^0 = U_1^0 \sigma(0) U_1^{0\dagger}. \tag{28}$$

For the pulse given above, $\sigma(0)=I_z$, $\beta_1^0=\pi/2$, $\mathbf{n}_1^0=\mathbf{n}_\pi$, $\beta_2^0=\pi$, $\mathbf{n}_2^0=\mathbf{n}_{5\pi/3}$, and the condition eqn.(27) may be shown to be fulfilled, as is demonstrated pictorially in the computer simulation of Fig.4. The residual z-magnetization has a cubic dependence on r.f. inhomogeneity $\delta\omega_1/\omega_1^0$, so the sequence is said to enjoy *second-order* compensation with respect to destruction of longitudinal magnetization.

Further development of these geometrical arguments led to a wide range of composite pulses with more highly compensated transformations of the initial condition. As examples of the more baroque developments we show in Fig.5. computer simulations of magnetization vector trajectories for (a) so-called 'spin-knotting' sequences[33]

$$(\beta_1^0)_{180} - \tau_1 - (\beta_2^0)_0 - \tau_2 - (\beta_3^0)_{180} \tag{29}$$

where $\beta_1^0=10°$, $\beta_2^0=60°$, $\beta_3^0=140°$, and τ_i represent small intervals of duration $\tau_1=0.8\pi/\omega_1^0$, $\tau_2=0.22\pi/\omega_1^0$; the sequence (29) provides a transformation $I_{kz} \rightarrow I_{ky}$ rather insensitive to offset effects, and (b) the sequence[36]

$$45_{90}90_{180}90_{270}45_{180}180_{270}45_{180}90_{90}90_{180}45_{270} \tag{30}$$

which provides a population inversion $I_{kz} \rightarrow -I_{kz}$ highly compensated for r.f. inhomogeneity.

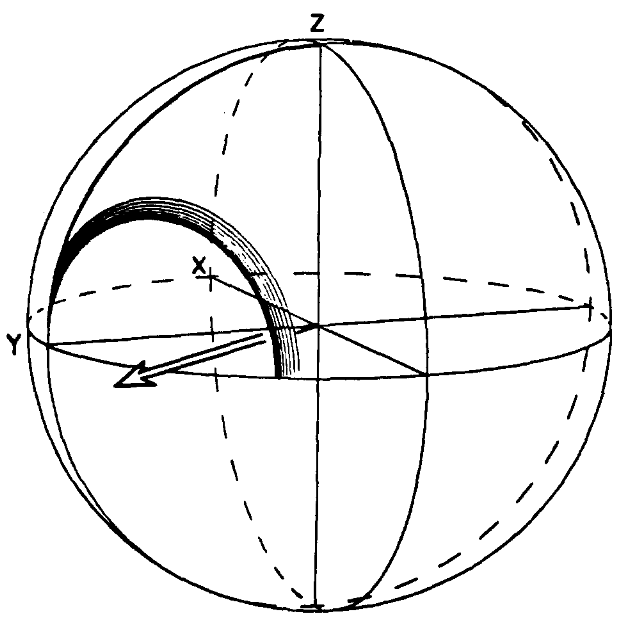

FIG. 4. Tracks traced out by a family of vectors experiencing on-resonance r.f. fields in the range $0.8 < \omega_1/\omega_1^0 < 1.0$ during the sequence $90_{180}180_{120}$. The rotation axis during the second pulse is indicated.

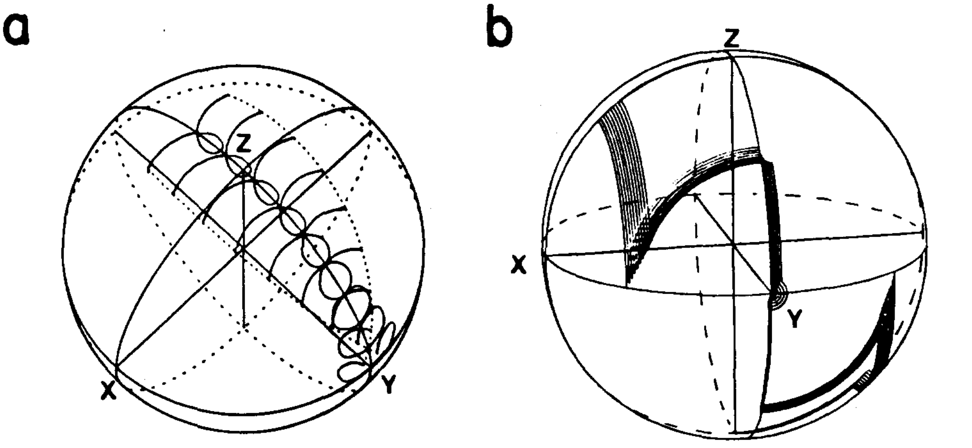

FIG. 5. Exotic suggestions for composite pulses. (a) 'Spin-knotting' sequence [eqn.(29)]; the plot shows the evolution in time of the locus formed by joining together the tips of a family of vectors experiencing off-resonance effects in the range $-0.5<\Omega/\omega_1^0<0.5$, taken at equal time increments through the second pulse in the sequence. Such plots are sometimes of assistance in gaining a physical insight into error compensation (from Ref.33). (b) Tracks of magnetization vectors experiencing on-resonance r.f. fields in the range $0.8<\omega_1/\omega_1^0<1.0$ during the 9-element composite 180° pulse given in eqn.(30). Highly compensated sequences such as this may be created with a combination of geometrical arguments and symmetry properties (from Ref.36).

3.2. *Propagator Compensation*; *Magnus Expansion*

The geometrical approach has the advantage of providing a strong physical picture of how error compensation works. Its disadvantages are that it is limited by the number of consecutive rotations which can be visualized, and that it is only easily possible to compensate the effect of a pulse sequence on a particular initial condition, usually a magnetization vector along the z-axis. The transformations of other initial conditions cannot easily be compensated at the same time and may not even suffer the desirable transformation under ideal conditions. For example, consider the sequence $90_{90}90_0$ which was shown above to provide a transformation of z-magnetization I_z into the xy plane insensitive to r.f. inhomogeneity effects. In the absence of non-idealities it transforms I_z to I_x and so might be thought to be equivalent to a 90_{90} pulse. That this is not the case is demonstrated by applying the sequence to another initial condition such as $\sigma(0)=I_y$. A 90_{90} pulse would leave I_y unchanged but $90_{90}90_0$ transforms I_y to I_z. Thus the sequence $90_{90}90_0$ may not be used to replace 90_{90} unless the initial condition is known to be I_z, or if special precautions are taken which are described later.

A way to ensure that not only the transformation of one particular initial condition is compensated, but also all the transformations of all possible initial conditions, is to concentrate on the compensation of the pulse sequence propagator U_p. If it can be ensured that $U_p \simeq U_p^0$ over a range of imperfections, where U_p^0 is the ideal propagator, then the pulse sequence may be used to replace the single pulse in all contexts.

As it is difficult to follow pictorially the transformations of all initial conditions at once, a more mathematical approach is indicated in this case. A suitable framework is provided by coherent averaging theory (also known as average Hamiltonian theory), which has been heavily used for high-resolution NMR in solids.[9,10]

We have already seen that for a time-independent Hamiltonian, the equation of motion (4) may be integrated over a time t to find the pulse sequence propagator $U(t)$, eqn.(6). During a pulse sequence, the Hamiltonian is only piecewise time-independent, so the propagator may be written as a product of terms for each pulse in the sequence, eqn.(8). This product of many non-commuting terms is not very meaningful unless the algebra of the operators can be used to reduce the product into a single, informative term. A way to do this in the special case of many consecutive rotations is in fact shown in the following Section. In this Section, a different direction is taken, which is to view the composite pulse as a special case of some time-dependent Hamiltonian $H(t)$ and to use an approximate expression for the integrated evolution operator. An appropriate expression is provided by the *Magnus expansion.* The integrated propagator for evolution over a time t under the time-dependent Hamiltonian $H(t)$ may be expressed

$$U(t)=\exp\{-i\bar{H}(t)t\}, \tag{31}$$

where the *effective Hamiltonian* $\bar{H}(t)$ is given as a power series in t:

$$\bar{H}(t)=\bar{H}^{(0)}(t)+\bar{H}^{(1)}(t)+\ \ldots \tag{32}$$

and

$$\begin{aligned}\bar{H}^{(0)}(t)&=t^{-1}\textstyle\int_0^t \mathrm{d}t' H(t')\\ \bar{H}^{(1)}(t)&=(2it)^{-1}\textstyle\int_0^t \mathrm{d}t'\int_0^{t'} \mathrm{d}t''[H(t'),H(t'')]\end{aligned} \tag{33}$$

Higher order expressions for $\bar{H}^{(2)}(t)$ etc., are given in Ref.(9,10); In general, $\bar{H}^{(m)}(t)$ is proportional to t^m.

This expansion is useful only if the series converges, so that higher order terms may be neglected. Conditions for convergence have been discussed in several places.[9,10,30,69] The condition most usually quoted, which, however, is not completely strict,[69] is that $\|H(t')t\| \ll 1$, which demands loosely that the duration over which the averaging is performed should be small enough that the Hamiltonian term H produces only a small change in the state of the system (weak perturbation case). Now it is clear from this that the Magnus expansion is not *directly* applicable to most pulse sequences, since the density operator changes very much throughout the sequence. However, this impasse may be avoided by a trick. Suppose the Hamiltonian can be divided into a 'big' part and a 'small' part:

$$H(t)=H_{\mathrm{big}}(t)+H_{\mathrm{small}}(t) \tag{34}$$

where usually the big part is 'simple and uninteresting' and the small part is 'complicated and interesting'. It is possible to pass into an *interaction frame* in which one 'moves with' the evolution due to the big part alone, so that this motion no longer affects the convergence of the expansion:

$$\tilde{\sigma}(t)=U_{\mathrm{big}}(t)^{\dagger}\sigma(t)U_{\mathrm{big}}(t) \tag{35}$$

$$\tilde{H}_{\mathrm{small}}(t)=U_{\mathrm{big}}(t)^{\dagger}H_{\mathrm{small}}U_{\mathrm{big}}(t) \tag{36}$$

and

$$\dot{\tilde{\sigma}}(t)=-i[\tilde{H}_{\mathrm{small}}(t),\tilde{\sigma}(t)] \tag{37}$$

In the interaction frame, most of the Hamiltonian is removed leaving only a small part $\tilde{H}_{\mathrm{small}}(t)$ given in eqn.(36). If H_{small} is small enough, the Magnus expansion now converges. Taking only the zeroth-order term in the expansion, the evolution of the density operator in the normal frame may be evaluated:

$$\sigma(t)=U(t)\sigma(0)U(t)^{\dagger} \tag{38}$$

where

$$U(t)=U_{\mathrm{big}}(t)\tilde{U}_{\mathrm{small}}(t) \tag{39}$$

$$\tilde{U}_{\mathrm{small}}(t)\simeq\exp\{-i\bar{H}^{(0)}_{\mathrm{small}}\ t\},$$

and

$$\bar{H}^{(0)}_{\mathrm{small}}\ t=\textstyle\int_0^t \mathrm{d}t'\tilde{H}_{\mathrm{small}}(t') \tag{40}$$

The main difficulty in using the Magnus expansion is to find the proper choice of the interaction frame which will ensure convergence. In high-resolution NMR in solids,[9,10] it is usual to choose for H_{big} the pulse sequence perturbations and for H_{small} the internuclear dipolar interactions and resonance offset terms; in heteronuclear decoupling in liquids,[11-15] the r.f. terms and chemical shifts have been taken together into H_{big}, leaving the heteronuclear coupling in H_{small}; in the presence of large resonance offsets it is even possible to have the r.f. pulse sequence in H_{small} and the offset in H_{big}.[30] We discuss here the choice made by Tycko *et al.*,[44,45,48] of having for H_{big} the Hamiltonian for an ideal pulse, and allowing H_{small} to include the residual Hamiltonian terms which may be held responsible for imperfect functioning of the pulse.

With this choice eqn. (39) has the following interpretation: $U_{\text{big}}(t)$ represents the propagator of an ideal pulse sequence. In the presence of non-idealities, this rotation should be preceded by a small rotation $\tilde{U}_{\text{small}}(t)$ of the initial condition. This rotation may be calculated through the *average Hamiltonian* $\bar{H}^{(0)}_{\text{small}}$ which represents the time-average of the pulse imperfections throughout the sequence, in the interaction frame. It is important to note the definition of the interaction frame, eqn. (35) as the frame which 'goes with' the motion induced by the ideal pulses. One may visualize this by 'sitting on' a magnetization vector and observing the rest of the world from this rotating reference point: If the rotations do not commute, this looks quite different to watching, from a static reference frame, the motion of a magnetization vector undergoing the same sequence of rotations. For example, the positions occupied by a vector starting at the z-axis under a sequence of rotations $90_0 90_{90}$ is $z \rightarrow -y \rightarrow -y$, but the positions occupied by the z-axis as viewed from the interaction frame are $z \rightarrow y \rightarrow -x$.

The operation of coherent averaging theory is easiest to visualize in calculating the performance of pulse sequences as a function of resonance offset, since in this case $H_{\text{small}}(t)$ is time-independent:

$$H_{\text{small}}(t) = \sum_k \Omega_k\, I_{kz} \tag{41}$$

Its motion in the interaction frame may easily be calculated. For example, consider a single 180_0 pulse:

$$\tilde{H}_{\text{small}}(t') = \sum_k \Omega_k (I_{kz}\cos(\omega_1^0 t') + I_{ky}\sin(\omega_1^0 t')) \tag{42}$$

Therefore

$$\bar{H}^{(0)}_{\text{small}}(t)t = \sum_k (\Omega_k/\omega_1^0) I_{ky} \tag{43}$$

using $\omega_1^0 t = \pi$.

The density operator after a 180° pulse applied to initial z-magnetization is therefore given approximately by eqn. (39):

$$\sum_k I_{kz} \xrightarrow{\tilde{U}_{\text{small}}(t)} \sum_k \{I_{kz}\cos(\Omega_k/\omega_1^0) + I_{kx}\sin(\Omega_k/\omega_1^0)\}$$
$$\xrightarrow{180_0^0} \sum_k \{-I_{kz}\cos(\Omega_k/\omega_1^0) + I_{kx}\sin(\Omega_k/\omega_1^0)\} \tag{44}$$

which is in agreement with eqn.(21), to first order in offset (Ω_k/ω_1^0). Of course this result is not too interesting for a single pulse but the arguments are readily extended to pulse sequences which are far too complicated for exact calculation. One only has to derive the motion of the interaction frame, which is not completely apparent in complicated cases, but is certainly calculable.

Coherent averaging theory may be used for designing composite pulses by setting $\bar{H}^{(0)}_{\text{small}}$, and hopefully also $\bar{H}^{(1)}_{\text{small}}$, close to zero, for the pulse imperfections embodied in the perturbation $H_{\text{small}}(t)$. The technique is to develop a set of simultaneous equations, with the pulse lengths and phases as variables, which define the conditions under which the various orthogonal components of $\bar{H}^{(n)}_{\text{small}}$ vanish. The equations are normally too difficult to be solved analytically, and numerical searches for an approximate solution must be conducted.

Tycko *et al.*[44,48] have devised a whole series of composite pulses on this basis. Sequences which have $\bar{H}^{(0)}$ and $\bar{H}^{(1)}$ close to zero for off-resonance effects are the composite 90° pulse

$$385_0 320_{180} 25_0 \tag{45}$$

and the composite 180° pulse

$$336_{27} 246_{207} 10_{117} 74_{287} 10_{117} 246_{207} 336_{27} \tag{46}$$

For r.f. inhomogeneity, $\bar{H}^{(0)}$ and $\bar{H}^{(1)}$ are made small by using the composite 90° pulse

$$270_{180} 360_{349} 180_{213} 180_{358} [70_z] \tag{47}$$

and the composite 180° pulse

$$180_{255} 180_0 180_{105} 360_{314} \tag{48}$$

where the phases have been adjusted so that the sequences produce overall rotations about the x-axis, and a 'supplementary z-rotation' has been introduced in sequence (47), indicating that the phases of all following pulses must be adjusted by $-70°$ if the composite pulse is to behave equivalently to 90_0 (see Section 4).

It is not immediately obvious how these sequences work 'physically' compared to the composite pulses described earlier. But they have the advantage that they may be applied without regard to the initial condition of the density operator and without thinking about the context of the pulse in the pulse sequence. This is a very important advantage, since it greatly simplifies the task of compensating a pulse sequence. However the pulses so far suggested do have some drawbacks which arise from their method of construction. Firstly, those compensated for r.f. inhomogeneity tend to have unusual phases—not an insuperable difficulty, but an inconvenience. Secondly, those compensated for off-resonance effects tend to have a rather modest range of compensation, although within that range they are very accurate (Section 4); the slow convergence of the Magnus expansion makes it difficult to extend the range of compensation of errors without greatly increasing the length of the sequence. Thirdly, the sequences tend to be rather sensitive to *simultaneous* r.f. inhomogeneity and resonance offset effects. Fourthly, a separate numerical optimization of pulse lengths and phases must be performed if it is required to create pulses having rotation angles different from 90° or 180°.

These drawbacks of the Magnus expansion pulses make it worthwhile considering if full compensation of the propagator is in fact necessary in the majority of experiments, and if a power-series expansion around a point of ideal behaviour is the most appropriate means of designing a pulse sequence for which brevity and bandwidth play at least as important a role as accuracy. The rest of this Section concerns composite pulses designed by a different approach, which although not enjoying full propagator compensation, have propagators compensated well enough for most requirements, whilst being rather short and easy to apply. The relative merits of the various sorts of composite pulse, and the situations in which it is possible to tolerate less than full compensation of the propagator, will be discussed further in Sections 4 and 5.

3.3. *Theory of Non-Commuting Rotations; Similarity Transformations*

Given one rotation through an angle β_1 about an axis $\mathbf{n}_1$, followed by a second rotation through an angle β_2 about an axis $\mathbf{n}_2$, through which angle and about which axis is the overall rotation? This question was asked and answered by Hamilton in the last century using his mathematical method of quaternions,[70] and interest in the solution has been revived recently in the context of composite pulses by Blümich and Spiess.[49] The answer to the question is by an angle β_{12} about an axis $\mathbf{n}_{12}$ given by

$$\begin{aligned} c_{12} &= c_1 c_2 - s_1 s_2 \mathbf{n}_1 \cdot \mathbf{n}_2 \\ s_{12} \mathbf{n}_{12} &= s_1 c_2 \mathbf{n}_1 + c_1 s_2 \mathbf{n}_2 - s_1 s_2 \mathbf{n}_1 \times \mathbf{n}_2 \end{aligned} \tag{49}$$

where $s_1 = \sin\beta_1/2$, $c_1 = \cos\beta_1/2$,etc.[40] A proof of this property using terminology familiar to the NMR community is given in Ref. (40). A solution may also be written down for three non-commuting rotations:

$$\begin{aligned}
c_{123} &= c_1c_2c_3 - (s_1s_2c_3\mathbf{n}_1\cdot\mathbf{n}_2 + s_1c_2s_3\mathbf{n}_1\cdot\mathbf{n}_3 + c_1s_2s_3\mathbf{n}_2\cdot\mathbf{n}_3) \\
&\quad + s_1s_2s_3(\mathbf{n}_1 \times \mathbf{n}_2)\cdot\mathbf{n}_3 \\
s_{123}\mathbf{n}_{123} &= s_1c_2c_3\mathbf{n}_1 + c_1s_2c_3\mathbf{n}_2 + c_1c_2s_3\mathbf{n}_3 \\
&\quad - (s_1s_2c_3\mathbf{n}_1 \times \mathbf{n}_2 + s_1c_2s_3\mathbf{n}_1 \times \mathbf{n}_3 + c_1s_2s_3\mathbf{n}_2 \times \mathbf{n}_3) \\
&\quad - s_1s_2s_3(\mathbf{n}_1(\mathbf{n}_2\cdot\mathbf{n}_3) - (\mathbf{n}_3\cdot\mathbf{n}_1)\mathbf{n}_2 + (\mathbf{n}_1\cdot\mathbf{n}_2)\mathbf{n}_3)
\end{aligned} \tag{50}$$

The above equations provide an exact alternative to the approximate coherent averaging theory in calculating the effect of a pulse sequence, although they often get too cumbersome to be used for more than two or three rotations. Nevertheless, a number of interesting properties of composite pulses can be derived analytically.[40]

We now consider some special cases of eqns.(49) and (50).

(a) Two small non-commuting rotations are applied ($\beta_1,\beta_2 \ll 1$). A series expansion of the overall rotation may be made:

$$\beta_{12}\mathbf{I}\cdot\mathbf{n}_{12} \simeq (\beta_1\mathbf{I}\cdot\mathbf{n}_1 + \beta_2\mathbf{I}\cdot\mathbf{n}_2) - \tfrac{1}{2i}[\beta_1\mathbf{I}\cdot\mathbf{n}_1,\ \beta_2\mathbf{I}\cdot\mathbf{n}_2] + \ldots \tag{51}$$

which is a special case of the Baker–Campbell–Hausdorff formula.[10] In the above, the property $[\mathbf{I}\cdot\mathbf{n}_1, \mathbf{I}\cdot n_2] = i\mathbf{I}\cdot(\mathbf{n}_1 \times \mathbf{n}_2)$ was used.

(b) Three rotations are combined, the first and last are exactly opposite ($\beta_1\mathbf{n}_1 = -\beta_3\mathbf{n}_3$) (rotation sandwich):

$$\begin{aligned}
\beta_{123} &= \beta_2 \\
\mathbf{I}\cdot\mathbf{n}_{123} &= \exp\{-i\beta_3\mathbf{I}\cdot\mathbf{n}_3\}\mathbf{I}\cdot\mathbf{n}_2\exp\{i\beta_3\mathbf{I}\cdot\mathbf{n}_3\}
\end{aligned} \tag{52}$$

These two properties take particular importance in the theory of composite pulses. The first because it shows how small rotations can be combined, and destructively interfere if $\beta_1\mathbf{n}_1 \simeq -\beta_2\mathbf{n}_2$. The second because it forms a way of manipulating the rotation axis of a given rotation whilst preserving the rotation angle, i.e. a *similarity transformation.* The property (b) above may also be proved using a formula often useful in the theory of NMR:

$$\exp(U\ A\ U^{-1}) = U\ \exp(A)\ U^{-1} \tag{53}$$

which is easily demonstrated by series expansion of the exponential.

Let us now concentrate on the practical implications of this latter property. Three practical cases of similarity transformations are significant.

(a) The actual 'sandwiching' of a given pulse by two pulses of opposite flip angle, in order to change its rotation axis. For example, if an ideal pulse $(\beta^0)^0_0$ is sandwiched by two ideal pulses 90^0_{90} and 90^0_{270}, the combination is by eqn. (52) equivalent to an ideal rotation through β^0 about the z-axis, $(\beta^0)^0_z$ (composite z-pulse[35]).

(b) An overall phase shift of a pulse or set of pulses is also a similarity transformation, since the rotation angle is left constant whilst the rotation axis is changed. The propagator may be thought to be sandwiched by two opposite z-rotations:

$$U_\phi = \exp\{-i\phi I_z\}U_{\phi=0}\exp\{i\phi I_z\}. \tag{54}$$

Compare also eqn. (20).

(c) The *cyclic permutation* of a pulse sequence element from one end of the composite pulse to the other also represents a similarity transformation. Suppose a sequence S exists with propagator $U(S)$ and which contains an initial sequence of pulses X which has a propagator $U(X)$. If X is removed from the beginning of S and reintroduced at the end (with no change in *its* order in time), the propagator for the permuted sequence (which can be denoted $X^{-1}SX$), is given by

$$U(X^{-1}SX) = U(X)\,U(S)\,U(X)^{\dagger}. \tag{55}$$

(Note the different chronological order in the sequence and the propagator.) Therefore if S produced a rotation by β_S about an axis $\mathbf{n}_S$, then the sequence $X^{-1}SX$ produces a rotation through the same angle β_S, but about a new axis $\mathbf{n}'$ modified by the action of X on $\mathbf{n}_S$:

$$\mathbf{I}\cdot\mathbf{n}' = U(X)\,\mathbf{I}\cdot\mathbf{n}_S\,U(X)^{\dagger} \tag{56}$$

We refer to rotations through the same angle but about different axes as *similar rotations*.

3.4. *Recursive Expansions*

The power of the above properties is that they show how to manipulate pulse sequences so as to produce well-defined effects on their overall propagators, to a large extent independent of their internal structure. This suggests methods of recursive expansion, in which any given pulse sequence is combined with its analogues derived by similarity transformation, to produce a longer sequence with more desirable properties than the original. The method is recursive because this new sequence may be in turn inserted into the machinery again to produce an even longer and even better sequence, and so on. Recursive properties can also be derived in the framework of coherent averaging theory,(14) but discussion tends to be much simpler in terms of similarity transformations of rotations. This point of view is supported by the contrast between Waugh's elegant and simple theory of heteronuclear decoupling(16,17) and the intricate coherent averaging theories which preceded it.(11–14)

3.4.1. *Broadband cycles.* Broadband cycles are composite pulses possessing vanishingly small overall rotation angles over a wide range of imperfections, especially resonance offset. At first sight it is not entirely clear to what use cyclic pulse sequences might be put, since they return irradiated spins to their initial state. In fact they are of great importance in themselves as heteronuclear decoupling sequences,(11–23) and also play a central role in the construction of more general composite pulses.

Two different recursive procedures are known for generating broadband cycles, involving cyclic permutation of either 180° pulses(14) or 90° pulses(17). Only the latter procedure will be discussed here, since it is generally recognized to converge more rapidly in the region of fairly small offsets and to yield more efficient cycles than the former.

The Waugh expansion(17) takes an initial approximation to a broadband cycle $C_0^{(m)}$, which provides a small rotation through an angle $\beta^{(m)}$, and produces a new cycle $C_0^{(m+1)}$ which is twice as long as $C_0^{(m)}$ but has a much smaller overall rotation angle $\beta^{(m+1)} \simeq \eta\beta^{(m)}$, where η is a convergence parameter, $\eta \ll 1$. A constraint is set upon the starting cycle $C_0^{(m)}$; for rapid convergence, $C_0^{(m)}$ should be of the form $C_0^{(m-1)}\,C_{180}^{(m-1)}$, i.e. it should itself consist of two cycles of opposite phase. This ensures that the rotation produced by $C_0^{(m)}$ is about an axis $\mathbf{n}_0^{(m)}$ close to the z-axis, $\mathbf{n}_0^{(m)}\cdot\mathbf{e}_z \simeq 1$.

The procedure runs as follows.

(a) Permute an element P_0 from the cycle $C_0^{(m)}$, to form the cycle $P_0^{-1}\,C_0^{(m)}\,P_0$.

(b) Shift the phase of the permuted cycle through 180° to give a cycle $P_{180}^{-1}\,C_{180}^{(m)}\,P_{180}$.

(c) Juxtapose the two similar rotations to yield

$$C_0^{(m+1)} = P_{180}^{-1}\,C_{180}^{(m)}\,P_{180}\,P_0^{-1}\,C_0^{(m)}\,P_0. \tag{57}$$

The cycle $C_0^{(m+1)}$ can then be used as input to step (a) again. It may be shown that convergence is usually better if on alternate steps of the expansion, the sense of cyclic permutations is reversed, i.e. if the first step follows the order in (a)–(c) above, then the next stage should employ back-to-front permutation, and the similar cycles should be juxtaposed in opposite order:

$$C_0^{(m+2)} = P_0\,C_0^{(m+1)}\,P_0^{-1}\,P_{180}\,C_{180}^{(m+1)}\,P_{180}^{-1}. \tag{58}$$

The element P_0 which is permuted is at best a broadband 90° pulse, i.e. it should transform I_z into the xy plane to a good approximation independent of offset. This condition is already fulfilled quite well for a single 90° pulse, $P_0 = 90_0$, eqn.(23). Assuming the cycle $C_0^{(m)}$ produces a rotation through an angle $\beta^{(m)}$ about an axis $\mathbf{n}_0^{(m)} = \mathbf{e}_z$, and that $\omega_1 = \omega_1^0$, then $P_0^{-1}\, C_0^{(m)}\, P_0$ rotates through $\beta^{(m)}$ about an axis close to the xy plane, defined in eqn.(22). The phase-inverted version $P_{180}^{-1}\, C_{180}^{(m)}\, P_{180}$ then rotates through the same small angle about an axis which is almost antiparallel, and by using eqn.(51), it is easy to show that $C_0^{(m+1)}$ produces a rotation through a smaller angle $\beta^{(m+1)}$ about an axis $n_0^{(m+1)}$ defined by

$$\beta^{(m+1)}\, \mathbf{I}\cdot\mathbf{n}_0^{(m+1)} = (1-\pi/4)\,(\Omega/\omega_1^0)^2\ \{2\beta^{(m)} I_z - (\beta^{(m)})^2 I_x\} \tag{59}$$

accurate to third order in offset (Ω/ω_1^0). For small $\beta^{(m)}$ the convergence parameter η is given by

$$\eta \simeq 2(1-\pi/4)(\Omega/\omega_1^0)^2. \tag{60}$$

Convergence is weaker if $C_0^{(m)}$ does not produce a rotation about the z-axis, $\mathbf{n}_0^{(m)} \neq \mathbf{e}_z$, and in this case the sense of permutation and juxtaposition on successive stages of the expansion also becomes important.

Waugh suggested building up broadband cycles based on the starting cycle $C_0^{(0)} = 360_0 360_{180}$ and demonstrated their favourable properties by computer simulation. Shaka *et al.*[20,21] made an important contribution by noting that since eqn. (60) ensures fast convergence anyway in the neighbourhood of $\Omega/\omega_1^0 \simeq 0$, cycles with wider broadband properties can be designed by using a starting cycle which is already perfect at some fairly large offset, and not worrying too much at its performance at small offsets. The faults at small offsets are rapidly corrected on expansion, whilst the good cyclic properties at large offsets are preserved. They chose instead the starting cycle $C_0^{(0)} = 270_0 270_{180}$, which is perfect ($\beta^{(0)} = 0$) at offsets $\Omega/\omega_1^0 = 0$ and $\pm 7^{1/2}/3$. Expansion of this cycle to order $C_0^{(4)}$ using the Waugh procedure yields a highly efficient broadband cycle called WALTZ-16[20,21] given by

$$\begin{aligned}
&270_{180}360_0 180_{180}270_0 90_{180}180_0 360_{180}180_0 270_{180} - \\
&270_0 360_{180}180_0 270_{180}90_0 180_{180}360_0 180_{180}270_0 - \\
&270_0 360_{180}180_0 270_{180}90_0 180_{180}360_0 180_{180}270_0 - \\
&270_{180}360_0 180_{180}270_0 90_{180}180_0 360_{180}180_0 270_{180}
\end{aligned} \tag{61}$$

which has a vanishingly small rotation angle over all offsets $-1.0 < \Omega/\omega_1^0 < 1.0$. (In fact the construction of WALTZ-16 does not follow the Waugh procedure completely logically, since the 'natural' second stage

$$C_0^{(2)} = 90_0 180_{180}270_0 90_{180}180_0 360_{180}180_0 270_{180}90_0 180_{180}270_0$$

was rearranged to give

$$C_0^{(2)} = 90_0 180_{180}360_0 180_{180}270_0 90_{180}180_0 360_{180}180_0 270_{180}$$

Whether this logical inconsistency has a noticeable effect on decoupling efficiency is not known.) Recently, additional variations on the theme have appeared, whch have been claimed to possess even larger cycle bandwidths than WALTZ-16.[22,23] A more thorough discussion of heteronuclear decoupling is beyond the scope of this article.

Very long cycles such as WALTZ-16 are not much use in the construction of composite pulse sequences. In this article we refer to the following short approximations to broadband cycles:

(i)	$360_0 360_{180}$	(62)
(ii)	$270_0 270_{180}$	(63)
(iii)	$180_{180}360_0 180_{180}360_0$	(64)

The first of these is a good cycle for small offsets. The second is a very rough cycle over an extended range, providing however up to 30 degree rotations at intermediate offsets. The third is a refined version of the second, much more accurate (errors only about 5 degrees) but twice as long. In addition, Starčuk *et al.*[50] have recently noted that cycles employing intermediate pulse lengths such as $285_0 285_{180}$ provide a compromise between these extremes. The properties of these broadband cycles are contrasted in Fig.6, which show contour plots of the overall rotation angles produced by the broadband cycles as a function of both r.f. field and resonance offset. For completeness, the performance of the long cycles[13]

$$R_0R_0R_{180}R_{180}R_0R_{180}R_{180}R_0R_{180}R_0R_0R_{180}R_{180}R_{180}R_0R_0$$

where

$$R_\phi = 90_\phi 240_{\phi+90} 90_\phi \tag{65}$$

and WALTZ-16 [eqn.(61)] are also shown.

3.4.2. *Recursive expansion of composite 90° pulses.* We now introduce a fourth similarity transformation of a pulse sequence, *inverse formation*[37], which like phase inversion and cyclic permutation, preserves the rotation angle of a sequence whilst changing the rotation axis. Forming the inverse of a pulse sequence involves finding another sequence which produces an exactly opposite rotation. If a sequence S has propagator $U(S)$, the inverse sequence S^{inv} is such that

$$U(S^{\mathrm{inv}}) \simeq (U(S))^\dagger = (U(S))^{-1} \tag{66}$$

It is clear that a sequence together with its inverse should form a cycle.

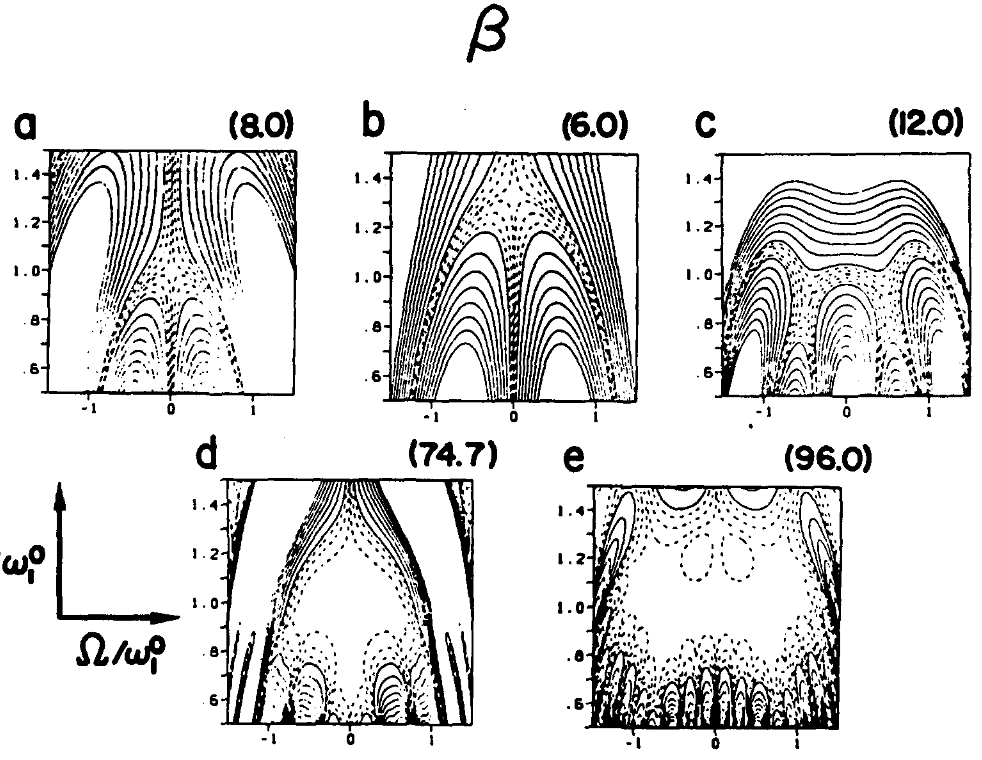

FIG. 6. Numerical evaluation of the overall rotation angle β produced by cyclic pulse sequences as a function of both r.f. field ω_1/ω_1^0 and resonance offset Ω/ω_1^0. Full contours run from 15° to 120° in units of 15°, broken contours are at 1°,5° and 10°. The sequences are (a) $360_0 360_{180}$; (b) $270_0 270_{180}$; this sequence is broadband but very inaccurate: (c) $180_0 360_{180} 180_0 360_{180}$; (d) 'MLEV-16' [eqn.(65)]; (e) 'WALTZ-16' [eqn.(61)]. The numbers in parentheses give the duration of the r.f. irradiation in units of a 90° pulse length.

If resonance offset effects may be neglected, the inverse of a sequence may be formed by applying the r.f. pulses in reverse order and with a shift of 180° in the phases:

If
$$S=(\beta_1^0)_{\phi_1}(\beta_2^0)_{\phi_2}(\beta_3^0)_{\phi_3}\ldots(\beta_p^0)_{\phi_p}$$
then
$$S^{\mathrm{inv}}=(\beta_p^0)_{\phi_p+180}\ldots(\beta_3^0)_{\phi_3+180}(\beta_2^0)_{\phi_2+180}(\beta_1^0)_{\phi_1+180} \tag{67}$$

If resonance offset effects may not be neglected, it is not possible to form the inverse exactly, except in some special cases where the sign of resonance offset is under control of the experimentalist through the application of static magnetic fields (this is the case in some imaging applications). Nevertheless a good approximation for the inverse is still available in the form of a *truncated broadband cycle.* Consider a broadband cycle C having an effective rotation angle β close to zero for a range of offsets. If the cycle contains a terminal element P, it may be considered to be formed from two unequal parts, CP^{-1} and P, with propagators related by

$$U(P)U(CP^{-1})\simeq 1 \tag{68}$$

Hence CP^{-1} is a good approximation to P^{inv}. Thus approximations to the inverse of a single 90_0 pulse are the sequences $360_{180}270_0$, $270_{180}180_0$, $180_{180}360_0180_{180}270_0$, etc.

Assuming an inverse may be found, a recursive expansion procedure is available for progressively refining the ability of some pulse sequence element $P_0^{(m)}$ to destroy z-magnetization:[37]

$$P_0^{(m+1)}=(P_{90}^{(m)})^{\mathrm{inv}}\,P_0^{(m)} \tag{69}$$

If resonance offset effects are neglected, application of this procedure to a starting sequence $P_0^{(0)}=90_0$ produces successively the expansions $P_0^{(1)}=90_{270}90_0$, $P_0^{(2)}=90_{270}90_{180}90_{270}90_0$, etc. The first of these was already discussed in a different way in Section 3.1. If resonance offset effects are present, sequences such as $P_0^{(1)}=(P_{90}^{(0)})^{\mathrm{inv}}\,P_0^{(0)}\simeq 360_{90}270_{270}90_0$[71] are called for. It should be remembered that if resonance offset effects are present, convergence of the procedure (69) is critically dependent on the accuracy of the inverse.

A simple rationalization of the procedure (69) may be given. Suppose $P_0^{(m)}$ represents some rotation which takes a vector from the z-axis to a position **n** close to the xy plane. The propagator for $P_0^{(m+1)}$ may be written

$$U(P_0^{(m+1)})\simeq U(P_0^{(m)})\exp(-i\tfrac{\pi}{2}I_z)U(P_0^{(m)})^{\dagger}\exp(i\tfrac{\pi}{2}I_z). \tag{70}$$

Neglecting the term on the right, $\exp(i\frac{\pi}{2}I_z)$, which is irrelevant if the sequence is applied to z-magnetization, eqn. (70) represents a similarity transformation of the propagator $\exp(-i\frac{\pi}{2}I_z)$ by $P_0^{(m)}$. Thus the rotation axis is moved from z to **n** near the xy plane. A 90° rotation about *this* axis provides a much more efficient destruction of z-magnetization than the original rotation $P_0^{(m)}$ (Fig.7). This is stated more mathematically in Ref.(37).

3.4.3. *Recursive expansion of 180° pulses.* It is also feasible to design recursion procedures which progressively refine the ability of composite 180° pulses to invert longitudinal vectors. If composite 180° pulses are denoted $R_0^{(m)}$, three of these procedures may be denoted[43,46,47]

$$R_0^{(m+1)}=R_0^{(m)}\,R_\phi^{(m)}\,R_0^{(m)} \tag{71}$$

where the value of ϕ is discussed below, and

$$R_0^{(m+1)}=R_0^{(m)}\,R_0^{(m)}\,R_{120}^{(m)}\,R_{60}^{(m)}\,R_{120}^{(m)} \tag{72}$$

$$R_0^{(m+1)}=R_0^{(m)}\,R_{330}^{(m)}\,R_{60}^{(m)}\,R_{330}^{(m)}\,R_0^{(m)} \tag{73}$$

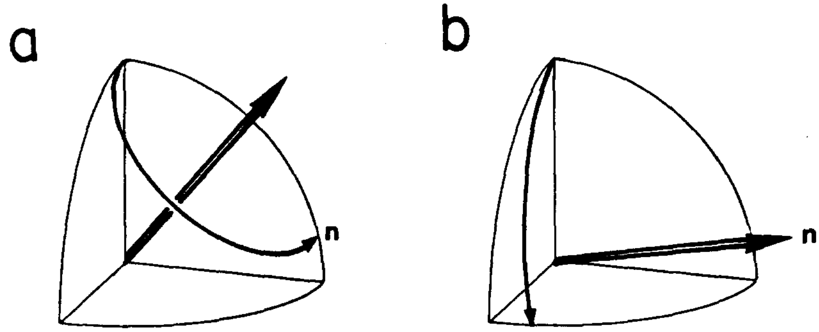

FIG. 7. Physical basis of the recursive expansion of composite 90° pulses. (a) An inaccurate sequence $P_0^{(m)}$ should rotate a vector from the z-axis to the xy plane, but the vector ends up at a position **n** instead. (b) The sequence $P_0^{(m+1)}$ defined in eqn.(69) produces a rotation by 90° about **n**, which gives a more accurate transformation of z into the xy plane.

For composite 180° pulses, a three- or five-fold expansion is indicated because the product of only an odd number of inversion operations is another inversion operation.

The three-fold expansion, eqn. (71) is applicable only to time-symmetrical sequences $R_0^{(m)}$,[40] whilst the five-fold expansions, eqn. (72) and (73) may be applied to any inversion pulse. Also, the three-fold expansion eqn. (71) produces enhanced performance only with respect to r.f. inhomogeneity, whilst the five-fold expansion makes no assumptions as to the form of the pulse imperfections.[47] Even pulse shape and phase transient errors may be compensated in this way.

All of these expansions may be rationalized using coherent averaging theory. However the most satisfying investigation of (71) was produced using the exact theory of non-commuting rotations as in Section. 3.3.[40] It was shown that if $R_0^{(m)}$ produces a rotation by an angle $\beta^{(m)}$ about an axis in the xy plane, then $R_0^{(m+1)}$ also produces a rotation about an axis in the xy plane but through an angle $\beta^{(m+1)}$ given by

$$\cos(\beta^{(m+1)}/2) = \cos\beta^{(m)}\cos(\beta^{(m)}/2) - \cos\phi\sin\beta^{(m)}\sin(\beta^{(m)}/2). \tag{74}$$

Now in the absence of off-resonance effects, a single pulse always produces a rotation about an axis in the xy-plane, and this property may be shown to be preserved by all time-symmetrical expansions.[40] In the case that $\phi = 120°$, deviations in $\beta^{(m)}$ from 180° are corrected to second-order:

$$\cos(\beta^{(m+1)}/2) = \cos^3(\beta^{(m)}/2). \tag{75}$$

The expansion eqn. (71) also has the versatile feature that 'coarse' adjustments of the properties of $R_0^{(m)}$ are available by setting $\phi \neq 120°$. For example, if $\phi = 90°$, then those r.f. fields for which the composite pulse $R_0^{(m)}$ performs so poorly that it destroys rather than inverts longitudinal magnetization give ideal performance for $R_0^{(m+1)}$.[43] This facility for coarse adjustment allows rapid progress towards sequences with very wide ranges of compensation. Starting from $R_0^{(0)} = 180_0$, the sequences

$$R_0^{(1)} = 180_0 180_{90} 180_0 \tag{76}$$

and

$$R_0^{(2)} = 180_0 180_{90} 180_0 180_{90} 180_{270} 180_{90} 180_0 180_{90} 180_0 \tag{77}$$

can be built up.[43] One stage of coarse adjustment with $\phi = 90°$ followed by one stage of fine adjustment with $\phi = 120°$ produces the highly compensated sequence[43]

$$R_0^{(2)} = 180_0 180_{90} 180_0 180_{120} 180_{210} 180_{120} 180_0 180_{90} 180_0 \tag{78}$$

The five-fold expansions, eqns.(72) and (73), are even more powerful because they make no assumptions at all about the form of the pulse imperfections or the sequences $R_0^{(m)}$. They were derived very elegantly by recognizing that an arbitrary rotation through an angle β about the axis $\mathbf{n}$ may be formed by juxtaposing two non-commuting rotations, both of which are about axes in the xy plane and one of which is through 180 degrees:[47]

$$\exp(-\beta\mathbf{I}\cdot\mathbf{n}) = \exp(-i\pi\mathbf{I}\cdot\mathbf{n}_\gamma)\exp(-i\varepsilon\mathbf{I}\cdot\mathbf{n}_\zeta). \tag{79}$$

Here $\mathbf{n}_\zeta\cdot\mathbf{e}_z = \mathbf{n}_\gamma\cdot\mathbf{e}_z = 0$ and the angles ε, ζ and γ are parametrically dependent on β and $\mathbf{n}$. Also, if $\exp(-i\beta\mathbf{I}\cdot\mathbf{n})$ is close to being a perfect inversion operation, then the angle ε is small. Using the property

$$\exp(-i\pi\mathbf{I}\cdot\mathbf{n}_\gamma)\exp(-i\varepsilon\mathbf{I}\cdot\mathbf{n}_\zeta) = \exp(-i\varepsilon\mathbf{I}\cdot\mathbf{n}_{\zeta'})\exp(-i\pi\mathbf{I}\cdot\mathbf{n}_\gamma) \tag{80}$$

where $\zeta' = 2\gamma - \zeta$, it is possible to show that expansions as in eqns.(72) and (73) cancel ε to first order. Tycko *et al.*[47] generated sequences up to and including $R_0^{(4)}$ (with 625 pulses) and demonstrated the spectacular insensitivity of such sequences to all types of pulse imperfection. A detailed investigation of the properties of such expansion procedures using the mathematical method if fixed-point analysis has recently appeared.[72]

3.5. *Transmutations of Composite Pulses*

Once a particular composite pulse has been created by one of the methods described above, it may often be transmuted into a different type of composite pulse by changing the phase of part of it, or by combining it with another sequence related through similarity transformation. An example has already been given: A broadband cycle may be transmuted into a broadband 90° pulse by changing the phase of a terminal 90° element by 90°. Other important transmutations are the following.

(i) A composite 90° pulse $P_0^{(m)}$ may be transmuted into a composite β pulse $(\beta)_0^{(m)}$ by juxtaposition with a similar sequence $(P_\beta^{(m)})^{\mathrm{inv}}$ derived by inverse formation and phase rotation by β:[37]

$$[(\beta)_z](\beta)_0^{(m)} = (P_\beta^{(m)})^{\mathrm{inv}}\, P_0^{(m)}. \tag{81}$$

In this equation, the composite pulse $(\beta)_0^{(m)}$ has been supplemented on the left by a rotation through β about the z-axis, indicating that if this pulse is introduced into a sequence, the phase of this pulse and of all subsequent pulses must be adjusted to take this into account, as discussed in Section 4. Including the z-rotation, the propagator for sequence (81) is given by

$$\begin{aligned} U(\beta_0^{(m)})\exp(-i\beta I_z) &= U(P_0^{(m)})\exp(-i\beta I_z)U(P_0^{(m)})^\dagger \\ &= \exp(-i\phi^{(m)}I_z)\exp(-i\beta I_x)\exp i\phi^{(m)}I_z) \end{aligned} \tag{82}$$

where $\phi^{(m)}$ is the phase of transverse magnetization produced by the sequence $P_0^{(m)}$ acting on z-magnetization, and assuming that $P_0^{(m)}$ is well enough compensated to ignore residual longitudinal components. The propagator of eqn.(82) corresponds exactly to a composite β pulse of phase $\phi^{(m)}$.

A special case of this procedure is when $\beta = 180°$. Then $P_0^{(m)}$ is transmuted into a composite 180° pulse. Examples neglecting off-resonance effects are the composite 180° pulses $R_0^{(1)} = 90_0 180_{90} 90_0$ and $R^{(2)} = 90_{270}90_{180}90_{270}180_0 90_{270}90_{180}90_{270}$, derived from $P_0^{(1)}$ and $P_0^{(2)}$ given in the previous Section. In the presence of off-resonance effects, pulses such as $270_0 180_{180} 90_0$[20,21] may be derived from $P_0^{(0)} = 90_0$ and $(P_0^{(0)})^{\mathrm{inv}} \simeq 270_{180}180_0$, and also higher-order composite pulses such as

$$\begin{aligned} R_0^{(1)} &= (P_{180}^{(1)})^{\mathrm{inv}}\, P_0^{(1)} \\ &= \{(P_{90}^{(0)})^{\mathrm{inv}}\, P_0^{(0)}\}_{180}^{\mathrm{inv}}\, \{(P_{90}^{(0)})^{\mathrm{inv}}\, P_0^{(0)}\} \\ &= (P_{180}^{(0)})^{\mathrm{inv}}\, P_{90}^{(0)}\, (P_{90}^{(0)})^{\mathrm{inv}}\, P_0^{(0)} \\ &\simeq 360_0 270_{180} 90_{90} 360_{270} 270_{90} 90_0, \end{aligned} \tag{83}$$

which is known under the name GROPE-16.[42] Higher-order expansions of this form have similar properties to the 5-fold expansions of the previous Section in that they are capable of compensating resonance offset effects and r.f. inhomogeneity effects at the same time, although their performance is strictly limited by the difficulty in forming short inverse sequences of usable accuracy.

(ii) If resonance offset effects are neglected, composite 180° pulses which are symmetrical in time may be transmuted into composite pulses of any flip angle β simply by shifting the first half of the sequence by β relative to the other half. For example it is possible to derive the composite 45° pulse

$$180_0 180_{90} 180_0 180_{120} 90_{210} 90_{255} 180_{165} 180_{45} 180_{135} 180_{45} \tag{84}$$

from the composite 180° pulse $R_0^{(2)}$ given in Ref.(43) and eqn.(78)

3.6. *Other Approaches to Composite Pulse Construction*

A few other ways have been suggested of constructing composite pulses. One of the more interesting ones arises from the group of Pines.[24] A class of *continuous* phase and amplitude modulation schemes may be devised with broadband inversion properties.[24,28-30] The principles of such modulation shapes are an extension of the theory of broadband 360° pulses which was worked out in optical spectroscopy especially in conjunction with the phenomenon of self-induced transparency[73] (The propagation of coherent pulses of particular shape through certain normally opaque media.) If the r.f. amplitude is constrained to be constant ($\omega_1 = \omega_1^0$), the phase modulation $\phi(t)$ which gives a broadband 180° pulse has been derived to be [24]

$$\phi(t) = \int_0^t \omega_1^0 \cos\gamma \tan\{(\omega_1^0 \sin\gamma)t'\}\, dt' \tag{85}$$

where the pulse extends from times $t = -T/2$ to $T/2$, over a total duration T given by

$$T = \pi/(\omega_1^0 \sin\gamma). \tag{86}$$

Here the parameter γ controls the degree of off-resonance compensation of the pulse; $\gamma = 90°$ leads to a conventional unmodulated 180° pulse with no compensation, whilst if γ approaches zero, the pulse becomes longer and acquires broadband properties.

For practical applications on conventional instruments, it has been suggested to approximate this smooth modulation scheme by a set of discrete pulses with different phases. This gives the composite 90° pulses[24] $84_{94} 251_0 84_{94}$, $64_{232} 122_{96} 310_0 122_{96} 64_{232}$, and $39_{329} 54_{209} 66_{139} 84_{70} 267_0 84_{70} 66_{139} 54_{209} 39_{329}$ (The last two sequences were printed incorrectly in Ref. (24).)

This method of generating composite pulses is of theoretical interest, but in practice has little to recommend it. The considerable length and inconvenient phases of the last two sequences are not compensated by their providing particularly spectacular bandwidths, and it is difficult to see how to generalize this approach to other types of composite pulse. However continous modulation schemes themselves rather than their discrete approximations probably will have a promising future. Some similar suggestions have been given by other workers.[28-30]

3.7. *Symmetry Properties*

It is often desirable to exploit symmetry arguments in determining the effect on a pulse sequence of transformations such as reversal of the order of the pulses in time, or reversing the sense of phase shifts. Symmetry arguments are also useful in deciding if the performance of the sequence depends on the sign of the offset from resonance. Most of the relevant properties may be deduced by considering the propagators for three different pulse sequences, called here A,B and C, which are related to each other through the following transformations.

(a) B is derived from A by reversal of the order of all pulses in time, retaining the sign of all phase shifts, so that

$$\phi_B(t) = \phi_A(\tau - t) \tag{87}$$

where τ is the duration of the sequence.

(b) C is derived from A by reversing the sense of all phase shifts, keeping the order in time, so that

$$\phi_C(t) = -\phi_A(t) \tag{88}$$

For example, if $A = 90_0 180_{120}$ then $B = 180_{120} 90_0$ and $C = 90_0 180_{240}$.

Neglecting as usual spin–spin couplings, it can be shown that the propagators for the three sequences are related by

$$U_B(\Omega) = \exp(-i\pi I_z)\; U_A(-\Omega)^{\dagger} \exp(i\pi I_z) \tag{89}$$

$$U_C(\Omega) = \exp -i\pi I_x)\; U_A(-\Omega) \exp(i\pi I_x) \tag{90}$$

where all propagators are expressed as functions of offset Ω.

As an example of the application of such expressions, consider a pulse sequence which is symmetrical in time ($A = B$) acting on an initial density operator $\sigma(0) = I_z$. The resultant z-magnetization as a function of offset is given by

$$\begin{aligned} \langle I_z \rangle^{+}(\Omega) &= Tr\{U_A(\Omega) I_z U_A(\Omega)^{\dagger} I_z\} \\ &= Tr\{U_A(\Omega)^{\dagger} I_z U_A(\Omega) I_z\} \\ &= Tr\{\exp(-i\pi I_z) U_A(-\Omega) \exp(i\pi I_z) I_z \exp(-i\pi I_z) U_A(-\Omega)^{\dagger} \exp(i\pi I_z) I_z\} \\ &= \mathrm{Tr}\{U_A(-\Omega) I_z U_A(-\Omega)^{\dagger} I_z\} \\ &= \langle I_z \rangle^{+}(-\Omega) \end{aligned} \tag{91}$$

using the invariance of the trace to cyclic permutation. Hence the z-magnetization after a time-symmetrical pulse sequence is independent of the sign of resonance offset.[36]

As a second example, consider a sequence containing pulses only of phases 0 or 180°. In this case $A = C$, and we have

$$\begin{aligned} \langle I_z \rangle^{+}(\Omega) &= Tr\{U_A(\Omega) I_z U_A(\Omega)^{\dagger} I_z\} \\ & Tr\{\exp(-i\pi I_x) U_A(-\Omega) \exp(i\pi I_x) I_z \exp(-i\pi I_x) U_A(-\Omega)^{\dagger} \exp(i\pi I_x) I_z\} \\ &= Tr\{U_A(-\Omega)(-I_z) U_A(-\Omega)^{\dagger}(-I_z)\} \\ &= \langle I_z \rangle^{+}(-\Omega). \end{aligned} \tag{92}$$

Hence here too, the z-magnetization is independent of the sign of resonance offset. This can also be demonstrated for $\langle I_y \rangle^{+}$. However $\langle I_x \rangle^{+}$ changes sign if the off-resonance term is inverted.

Many more relationships on similar lines may be derived. A further example which has already been mentioned is that the overall rotation produced by a time-symmetrical sequence applied on resonance is about an axis in the xy-plane.[40] Additional symmetry properties are encountered when composite pulses are applied to dipolar-coupled systems; the expectation value of any angular momentum component after an arbitrary pulse sequence applied to z-magnetization is independent of the sign of the couplings.[45]

3.8. *Far Off-Resonance Behaviour*

Most of the composite pulses so far described have been designed with the intention of applications in high-resolution NMR, where resonance offsets are usually of the order of the r.f. field strength. However there are a number of potential applications within and outside NMR in which behaviour far from resonance is of interest. An example is selective excitation, where weak composite pulses could be used to provide a flat frequency response over some band of resonances. This would be particularly useful in NMR imaging, since it would allow uniform excitation within a flat slice selected by a static magnetic field gradient. Applications of composite pulses are also conceived in coherent laser spectroscopy.(74–76) Here the considerable inhomogeneous broadening of many lasers compared to the strength of the interaction between the electric field and typical electronic transitions also provides large off-resonance effects.

Warren has shown by using a form of coherent averaging theory that sufficiently far from resonance, the effect of arbitrary pulse sequences is proportional to the Fourier transform of the excitation.(30) Thus the linear approximation, which we emphasized above to be very poor near to resonance, regains its validity if offsets become large. (This needs some qualification in the light of the demonstration of high-order NMR resonances in the case of suitably modulated r.f. fields, which show that even for weak irradiation with no Fourier components close to resonance, strong non-linear perturbations of the spin system may result.(77–78) However these 'multiple-photon effects' need considerable time to develop and can usually be ignored.) The resurrection of the linear approximation at high offsets is bad news as far as the direct application of composite pulses is concerned, since the sudden phase shifts involved in composite pulses give wild oscillations in the frequency spectrum far from resonance. Hence smooth modulation of amplitude and phase is called for in developing frequency-selective pulses, rather than the discrete modulation schemes discussed above.(24–31) This of course does not rule out many useful applications in NMR imaging where excitation or inversion of all spins in the sample can be achieved using strong composite pulses. Also, it might be possible to round the shapes of composite pulses so as to remove the oscillatory characteristics far from resonance without perturbing too much the good behaviour at small offsets.

4. CLASSIFICATION AND PROPERTIES OF COMPOSITE PULSES

4.1. *Classification*

We have seen in the previous Section that there are numerous methods for creating composite pulses, based on different theoretical approaches. It is not surprising that the different approaches give rise to composite pulses with different properties. To ease discussion of the way in which composite pulses can be introduced into a multiple-pulse NMR experiment, we now introduce a system of classification according to the transformation properties of the pulse sequences.

We assign composite pulses to four classes, which we call A, B1, B2 and B3. The characteristic features of the four classes are as follows.

(a) Composite pulses of type A produce, over a particular range of imperfections, a *fully compensated rotation* of the system, so that

$$U_p \simeq U_p^0. \tag{93}$$

This implies that, within some approximation, all initial states of a spin system are rotated to what their values would be after an ideal pulse. Hence this type of composite pulse is the most versatile of all. Numerical optimization with the help of coherent averaging theory seems best suited for creating this type of composite pulse.(44,45,48)

Composite pulses of type B, on the other hand, do not enjoy such full compensation of the propagator, so the compensation effect depends somewhat on the initial condition of the spin ensemble and the tolerance of the particular experiment to phase errors. We define the properties of the sub-types B1,B2 and B3 as follows.

(b) Composite pulses of type B1 produce, over a range of imperfections, a partially compensated rotation such that

$$U_p \simeq \exp(-i\textstyle\sum_k \varepsilon_k I_{kz})\, U_p^0 \,\exp(i\textstyle\sum_k \varepsilon_k I_{kz}). \tag{94}$$

Thus the compensated propagator differs from the ideal propagator only by an overall phase shift, which may be dependent on the pulse imperfections, and in the case of off-resonance effects, may differ from spin to spin. The theory of composite pulses discussed in Sections 3.3 to 3.6 often creates this type of composite pulse.

(c) Composite pulses of type B2 enjoy a compensated transformation of one particular initial condition, usually I_z, to one particular final condition, i.e.

$$U_p I_z U_p^{\dagger} \simeq U_p^0 I_z U_p^{0\dagger}. \tag{95}$$

The transformations of other initial conditions may not even resemble the ideal ones.

(d) Composite pulses of type B3 give again a compensated transformation of one particular initial condition, but the phase of the final density operator is not compensated and may depend on the imperfections, i.e.

$$U_p I_z U_p^{\dagger} \simeq \exp(-i\textstyle\sum_k \varepsilon_k I_{kz}) U_p^0 I_z U_p^{0\dagger} \exp(i\textstyle\sum_k \varepsilon_k I_{kz}). \tag{96}$$

As examples of these last two categories, composite 90° pulses often produce compensated transformations $I_z \rightarrow -I_y$(category B2) or $I_z \rightarrow \mathbf{I}\cdot\mathbf{n}_{\phi}$ (category B3; ϕ is arbitrary). In general, the more pictorial approaches to composite pulse design tend to produce partially compensated rotations of these last two types.

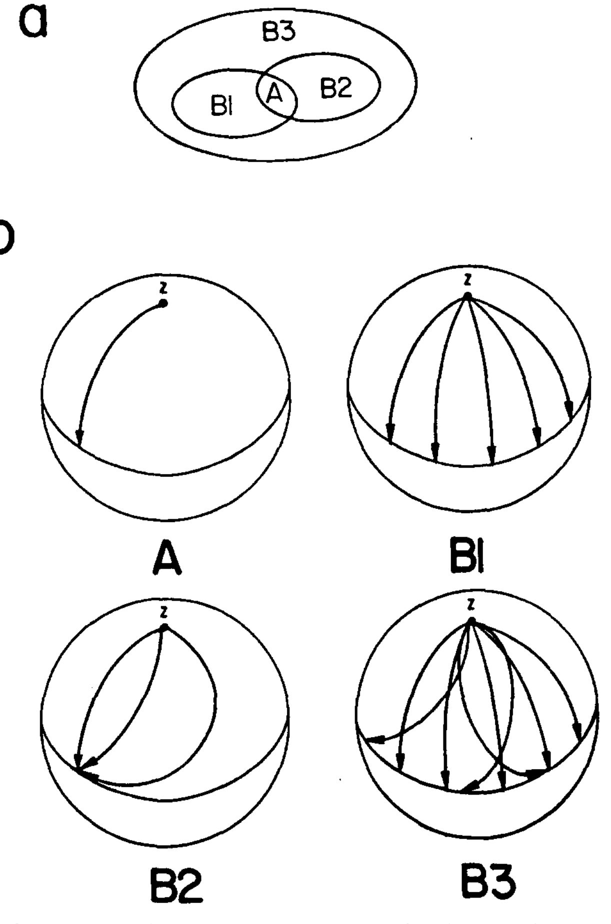

FIG. 8. Classification of composite pulses. (a) Venn diagram showing the mutual membership of classes A, B1, B2 and B3. (b) The types of transformation belonging to the four classes for a composite 90° pulse. Class A contains only ideal transformations through 90° about a defined axis in the xy plane. Class B1 tolerates phase deviations in the rotation axis. Class B2 is concerned only with the transformation of one particular initial condition to one particular final condition, the rotation not being uniquely defined. Class B3 also tolerates phase errors in this final condition.

The four classes are not mutually exclusive; for example, a composite pulse of class A also simultaneously belongs to B1, B2 and B3 as well. The Venn diagram of Fig. 8a is intended to clarify this. Fig.8b shows, for a composite 90° pulse, the different types of rotation which can be accommodated in the four categories.

For composite 180° pulses, a simplification takes place because the only rotations which produce a transformation $I_z \rightarrow -I_z$ are of the form

$$\exp(-i\textstyle\sum_k \varepsilon_k I_{kz})\exp(-i\pi\sum_k I_{kx})\exp(i\sum_k \varepsilon_k I_{kz}). \tag{97}$$

i.e. 180° rotations about axes in the xy plane. Thus all classes B1, B2 and B3 share the same members in this case, and composite 180° pulses may be termed B-type without ambiguity (Fig. 9).

4.2. *Comparison of Composite Pulses*

In Tables 1–2 we group most of the useful known 90° and 180° composite pulses into the four categories presented above. A subjective judgement as to whether the compensation is 'low' 'moderate' or 'high' is also given. This will be placed on a more quantitative basis in a moment. For many of the pulses in categories A or B1, a supplementary z-rotation has been appended to the pulse sequence. This indicates that the overall propagator of the sequence must include an ideal additional rotation about the z-axis. In practice phase adjustments of subsequent pulses are necessary in order to take account of this as is discussed in Section 4.3.2.

Dieter Suter of the ETH-Zürich has kindly made available a PASCAL computer program for numerical simulation of composite pulses. The program calculates the overall rotation angle β and axis $\mathbf{n}$ generated by a composite pulse in the presence of simultaneous r.f. inhomogeneity and resonance offset effects by application of Hamilton's eqn.(49) to the propagators defined in eqns.(18). The overall rotation may then be compared with an ideal rotation, or applied to I_z and the transformed density operator examined. Parameters of interest may then be displayed as contour plots against the two parameters Ω/ω_1^0 and ω_1/ω_1^0. In the diagrams discussed below, all contour plots are drawn with full contours spaced at 0.2 intervals and dotted contours appearing at ± 0.9 ± 0.95 and ± 0.99.

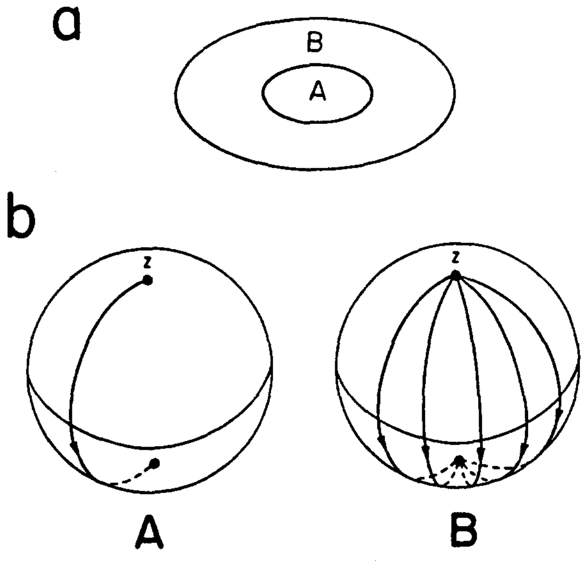

FIG. 9. In the special case of a composite 180° pulse, classes B1, B2 and B3 coalesce.

TABLE 1. Composite 90° pulses

		Category			
		A	B1	B2	B3
r.f. field compensation	high		$[90_z]90_{180}90_{90}90_{0}90_{90}90_{180}90_{90}90_{180}90_{270}$		$270_{180}360_{349}180_{213}180_{358}$ $90_{0}180_{105}180_{315}$
	medium	$270_{180}360_{349}180_{213}180_{358}[70_z]$ $90_{0}180_{105}180_{315}[-60_z]$	$270_{180}360_{349}180_{213}180_{358}[70_z]$ $90_{0}180_{105}180_{315}[-60_z]$	$270_{180}360_{349}180_{213}180_{358}$ $90_{0}180_{105}180_{315}$	$90_{300}180_{60}$
	low		$[90_z]90_{90}90_{0}90_{90}90_{180}$	$90_{300}180_{60}$ $45_{90}90_{0}90_{270}45_{0}$	$90_{90}90_{0}$
Resonance offset compensation	high		$[90_z]180_{0}360_{180}180_{0}270_{180}90_{90}$		$180_{0}360_{180}180_{0}270_{180}90_{90}$
	medium	$385_{0}320_{180}25_{0}$	$385_{0}320_{180}25_{0}$	$385_{0}320_{180}25_{0}$	$360_{0}270_{180}90_{90}$ 90_{0} $385_{0}320_{180}25_{0}$
	low				
Simultaneous r.f. field and resonance offset compensation	high				
	medium				$180_{0}360_{180}180_{0}270_{180}90_{90}$ $360_{0}270_{180}90_{90}$
	low				

TABLE 2. Composite 180° pulses

		Category	
		A	B
r.f. field compensation	high		$180_0 180_{90} 180_0 180_{120} 180_{210} 180_{120} 180_0 180_{90} 180_0$ $180_0 180_{105} 180_{210} 360_{59}$
	medium	$180_0 180_{105} 180_{210} 360_{59}$	$90_{90} 90_0 90_{270} 180_0 90_{270} 90_0 90_{90}$ $90_0 360_{120} 90_0$ $180_0 180_{120} 180_0$
	low	$180_0 180_{120} 180_0$	$90_{90} 180_0 90_{90}$
Resonance offset compensation	high		$180_0 360_{180} 180_0 270_{180} 90_0$ $90_0 200_{90} 80_{270} 200_{90} 90_0$
	medium	$336_0 246_{180} 10_{90} 74_{270} 10_{90} 246_{180} 336_0$	$90_0 180_{180} 270_0$
	low		$90_{90} 240_0 90_{90}$ $90_{90} 180_0 90_{90}$ $90_0 225_{180} 315_0$
Simultaneous r.f. field and resonance offset compensation	high		Tycko 25-pulse sequence[47]
	medium		$360_0 270_{180} 90_{90} 360_{270} 270_{90} 90_0$
	low		$360_0 180_{120} 180_{60} 180_{120}$

4.2.1. *Composite 90° pulses*

In Figs 10–18 we examine the performance of various composite 90° pulses according to criteria appropriate to categories A, B1, B2 and B3.

(a) For category A the rotation produced by the composite pulse should be compared with an ideal 90_0 rotation. The question arises as to how to compare quantitatively two rotations as abstract entities, without referring to the transformation of a particular initial condition. A suitable framework is provided by quaternions,[49] which are four-dimensional unit vectors with elements related to the rotation angle β and rotation axis $\mathbf{n}$ of a rotation operator by

$$\mathbf{q} = \{\cos(\beta/2), \mathbf{n}\cdot\mathbf{e}_x\sin(\beta/2), \mathbf{n}\cdot\mathbf{e}_y\sin(\beta/2), \mathbf{n}\cdot\mathbf{e}_z\sin(\beta/2)\} \tag{98}$$

It seems reasonable to take as a measure of the deviation of a rotation from ideality the scalar product of its quaternion with the quaternion for an ideal rotation; this has unit magnitude if the rotation is ideal and less than unity for an ideal rotation (if the scalar product is -1, this also indicates an ideal rotation; for example the ideal rotations 90_0^0 and 270_{180}^0 are to be counted as the same thing). For an ideal 90_0 pulse the quaternion is

$$\mathbf{q}^0 = \{2^{-1/2}, 2^{-1/2}, 0, 0\} \tag{99}$$

so the quantity

$$\lambda = |\mathbf{q}\cdot\mathbf{q}^0| = 2^{-1/2}|\cos(\beta/2) + \mathbf{n}\cdot\mathbf{e}_x\sin(\beta/2)| \tag{100}$$

is used as a measure of the ideality of composite 90° pulses of type A.

(b) For composite pulses of type B1, the quaternion for the composite pulse should also be compared with the quaternion for an ideal rotation, but this time the phase of the rotation may be ignored. A parameter λ' is used, given by

$$\lambda' = 2^{-1/2}\{|\cos\beta/2| + |\sin\beta/2|[(\mathbf{n}\cdot\mathbf{e}_x)^2 + (\mathbf{n}\cdot\mathbf{e}_y)^2]^{1/2}\}. \tag{101}$$

This parameter is again unity for an ideal rotation, and less than unity for a non-ideal rotation.

(c) Composite 90° pulses must be judged in category B2 according to the y-magnetization produced by the sequence when it is applied to I_z:

$$\langle I_y\rangle^+ = Tr\{\exp(-i\beta\mathbf{I}\cdot\mathbf{n})\, I_z \exp(i\beta\mathbf{I}\cdot\mathbf{n})\, I_y\}/Tr\{I_y{}^2\}. \tag{102}$$

The y-magnetization is -1 for an ideal rotation, and greater for a non-ideal rotation.

(d) Category B3 differs from category B2 in that the phase of the transverse magnetization is ignored. The relevant parameter is $\langle I_{xy}\rangle^+$ given by

$$\langle I_{xy}\rangle^+ = \{(\langle I_x\rangle^+)^2 + (\langle I_y\rangle^+)^2\}^{1/2} \tag{103}$$

which is one for an ideal rotation.

A single 90_0 pulse and four composite pulses are compared on the basis of parameter λ in Fig.10. Two of the composite pulses were designed by coherent averaging theory[48] to give r.f. field compensation. That this was successful is revealed by the elongation of the region of ideal performance in the vertical direction in the contour plots. The performance of the sequence $385_0 320_{180} 25_0$ designed by coherent averaging theory so as to give off-resonance compensation, is also shown and indeed displays a moderate elongation of the dotted contors in the horizontal direction. For comparison, the performance of the sequence $[90_z]180_0 360_{180} 180_0 270_{180} 90_{90}$ is also shown. This was derived by the different approach of Section 3.4. This method of generating composite pulses does not give a fully-compensated propagator, as is revealed in the diagram which does not show a noticeable widening of the region of good performance.

If the phase of the propagator is ignored, as in category B1, the relative merits of these sequences appear somewhat different. In Fig. 11 the parameter λ' is shown which is calculated for a single 90_0 pulse and five composite pulses, three with r.f. field compensation and two with offset compensation. The three pulses derived by coherent averaging theory retain their previous ranges of compensation, but they now have competition in the form of the r.f. field compensated sequence[37]

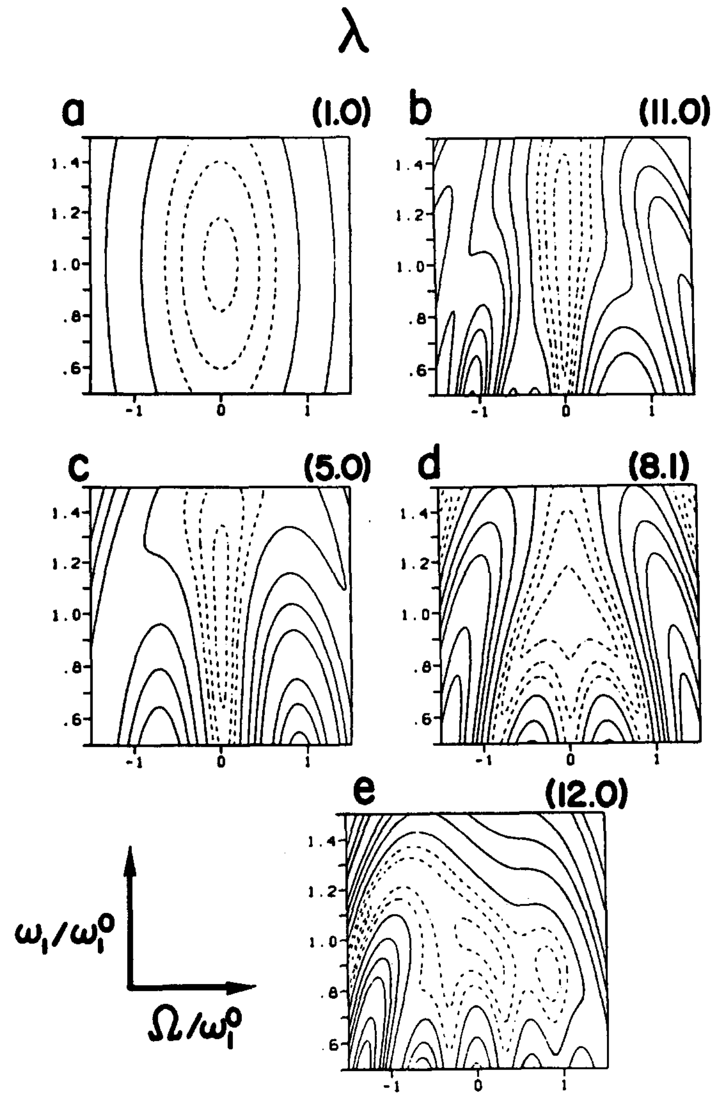

FIG. 10. Numerical evaluation of composite 90° pulses according to the parameter λ [eqn.(100)], appropriate for A-type composite pulses. Full contours in 0.2 intervals, dotted contours at ± 0.9, ± 0.95, ± 0.99. The sequences are (a) 90_0, the r.f. field compensated pulses (b) $270_{180}360_{349}180_{213}180_{358}[70_z]$,[48] (c) $90_0 180_{105} 180_{315}[-60_z]$,[48] and the resonance offset compensated pulse (d) $385_0 320_{180} 25_0$.[48] The sequence (e) $[90_z]180_0 360_{180} 180_0 270_{180} 90_{90}$[37,71] is also shown, but does not display compensation. Overall durations in units of a 90° pulse are given in brackets.

$[90_z]90_{180}90_{90}90_0 90_{90}90_{180}90_{90}90_{180}90_{270}$ and the offset-compensated sequence[37,71] $[90_z]180_0 360_{180} 180_0 270_{180} 90_{90}$. These latter two may be generated by the methods of Section 3.4, and have very wide compensation bandwidths if the phase of the propagator is ignored.

When the y-magnetization generated is the criterion of ideality (category B2), different possibilities again exist (Fig. 12). The three coherent averaging sequences again perform well. For r.f. field compensation, the simple sequences $90_{300}180_{60}$ and $45_{90}90_0 90_{270}45_0$ created by simple geometric arguments [36] should also be considered. Their ranges of compensation are modest, but they are not too sensitive to resonance offsets.

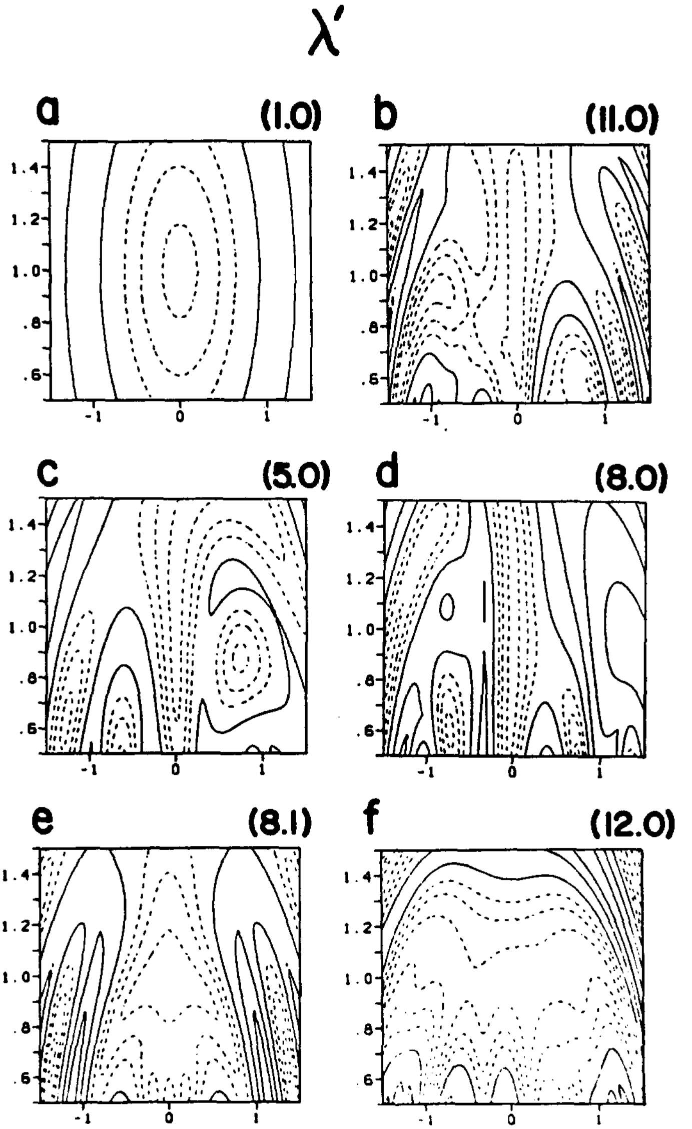

FIG. 11. Numerical simulations of composite 90° pulses according to the parameter λ' [eqn.(101)], appropriate for B1-type composite pulses. The sequences are (a) 90_0, the r.f. field compensated pulses (b) $270_{180}360_{349}180_{213}180_{358}[70_z]$,(48) (c) $90_0 180_{105}180_{315}[-60_z]$,(48) (d) $[90_z]90_{180}90_{90}90_0 90_{90}90_{180}90_{90}90_{180}90_{270}$,(37) and the offset compensated pulses (e) $385_0 320_{180}25_0$,(48) (f) $[90_z]180_0 360_{180}180_0 270_{180}90_{90}$.(37,71)

If the phase of the transverse magnetization may be ignored (category B3), the selection is wider again, as is shown in Fig.13 and 14. It is apparent that a single 90_0 pulse already has only a weak offset-dependence when judged by $\langle I_{xy}\rangle^+$, as is well-known. Four sequences are also shown with r.f. field compensation, the coherent averaging sequences $90_0 180_{105}180_{315}[-60_z]$ and $270_{180}360_{349}180_{213}180_{358}[70_z]$(48) being among them. These two are highly compensated, but rather offset-sensitive. The simple sequences $90_0 90_{90}$ and $90_{300}180_{60}$(33-36) also display considerable r.f. field compensation when judged by $\langle I_{xy}\rangle^+$. For off-resonance compensation, $385_0 320_{180}25_0$(48) is superior to 90_0 only for very small offsets.

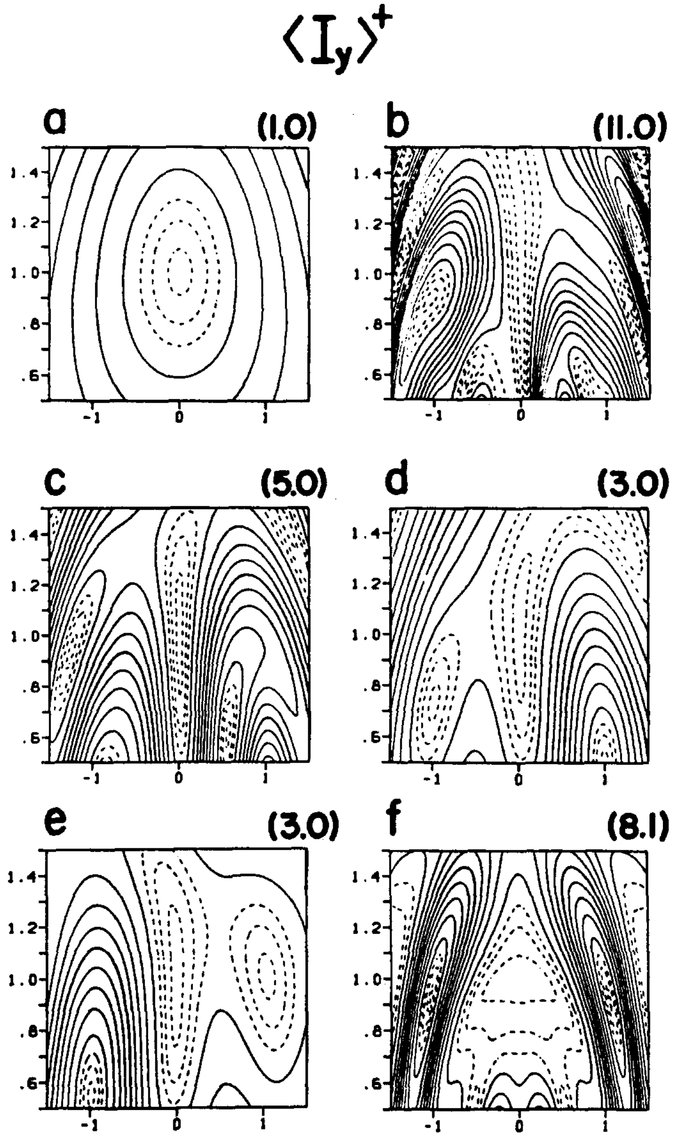

FIG. 12. Numerical evaluation of composite 90° pulses according to $\langle I_y \rangle^+$, appropriate for B2-type composite pulses. The sequences are (a) 90_0, the r.f. compensated pulses (b) $270_{180}360_{349}180_{213}180_{358}[70_z]$,[48] (c) $90_0180_{105}180_{315}[-60_z]$,[48] (d) $90_{300}180_{60}$,[36] (e) $45_{90}90_0 90_{270}45_0$,[36] and the offset-compensated pulse (f) $385_0 320_{180}25_0$.[48]

The sequences $360_0 270_{180}90_{90}$ and $180_0 360_{180}180_0 270_{180}90_{90}$[37,71] (Section 3.4) give some measure of simultaneous r.f. field and resonance offset compensation.

4.2.2. *Composite 180° pulses.* In Figs 15–18 we compare the large number of composite 180° pulses which have been suggested, in this case for simplicity only according to the degree of inversion of longitudinal magnetization, $\langle I_z \rangle^+$. As in the previous calculations, the contours are given in 0.2 units from -0.8 to 0.8, with dotted contours at -0.9, -0.95 and -0.99 appearing in the region of ideal behaviour.

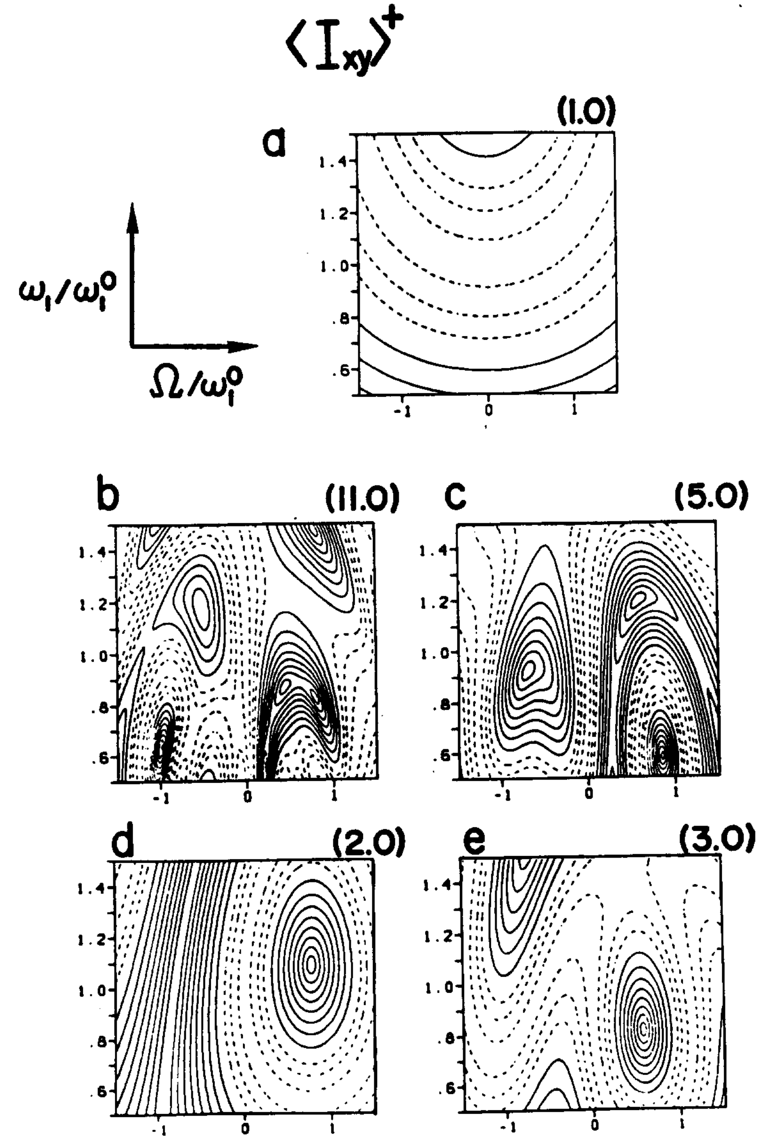

FIG. 13. Numerical evaluation of composite 90° pulses according to $\langle I_{xy} \rangle^+$, appropriate for type B3. The sequences are (a) 90_0, and the r.f. compensated sequences (b) $270_{180}360_{349}180_{213}180_{358}[70_z]$,[48] (c) $90_0180_{105}180_{315}[-60_z]$,[48] (d) $90_{90}90_0$,[33] (e) $90_{300}180_{60}$.[36]

Figure 15 shows the performance of a single 180° pulse, compared with three-element composite pulses of the form $90_0\beta^0_{90}90_0$. The roughly T-shaped form of the contours in Fig. 15b shows that $90_0180_{90}90_0$ compensates either small r.f. field errors *or*, to some extent, resonance offsets, although compensation of the latter is not very precise. Resonance offset compensation is made more accurate by increasing the length of the central pulse, at the expense of bandwidth.[32–34] The sequence $90_0270_{90}90_0$ has $\bar{H}^{(0)}=0$ for off-resonance effects.[44]

Figure 16 shows the outcome of various attempts to improve the r.f. field compensation. Displayed is the calculated performance of the sequences $90_0360_{120}90_0$,[36] $90_{90}90_090_{270}180_0$

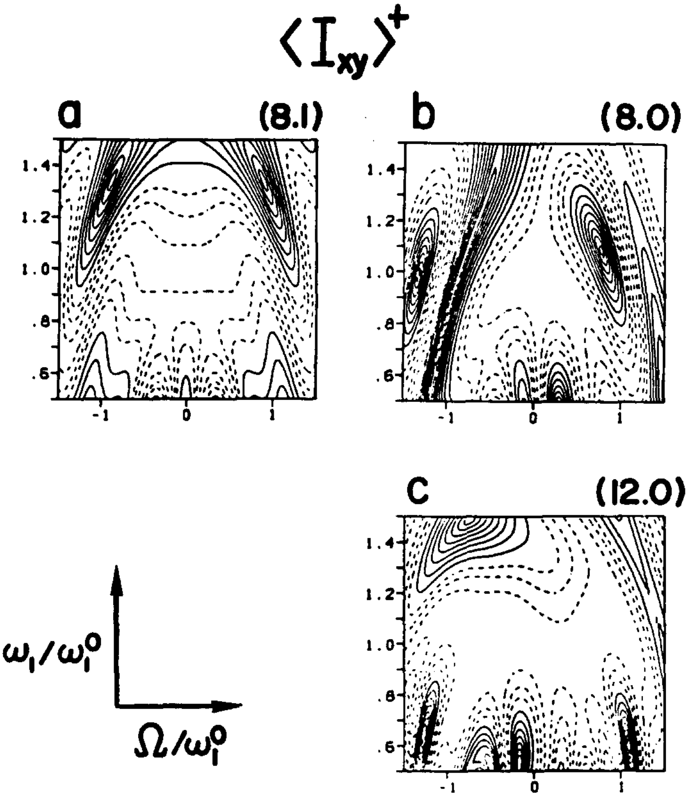

FIG. 14. Evaluation of composite 90° pulses according to $\langle I_{xy}\rangle^+$, appropriate for B3-type sequences. The offset-compensated composite pulses are (a) $385_0 320_{180} 25_0$,[48] (b) $360_0 270_{180} 90_{90}$,[37,71] and (c) $180_0 360_{180} 180_0 270_{180} 90_{90}$.[37,71]

$90_{270} 90_0 90_{90}$,[37] $180_0 180_{120} 180_0$,[44] and the expanded sequences $180_0 180_{90} 180_0 180_{120} 180_{210} 180_{120} 180_0 180_{90} 180_0$[43] and $180_0 180_{105} 180_{210} 360_{59}$.[48] The range of compensation of the last two is clearly very large, but this is at the expense of a high sensitivity to resonance offset. A striking feature of the first three sequences is that although they were constructed using quite different principles, their performance is very similar.

Sequences with improved resonance offset compensation are compared in Fig.17. The sequences $90_0 200_{90} 80_{270} 200_{90} 90_0$,[36] $39_{329} 54_{209} 66_{139} 84_{70} 267_0 84_{70} 66_{139} 54_{209} 39_{329}$,[24] $90_0 180_{180} 270_0$ and $180_0 360_{180} 180_0 270_{180} 90_0$[20,21] all give wider bandwidths, but also without being very accurate. The last two have the important feature, however, that they involve only 180° phase shifts, making them very suitable for heteronuclear decoupling,[20,21] or after division of all pulse lengths by two, for spin $I = 1$ NMR[39] (see below). The accuracy of the spin inversion can again be improved at the expense of bandwidth by using the sequences $90_0 225_{180} 315_0$[50] or $336_0 246_{180} 10_{90} 74_{270} 10_{90} 246_{180} 336_0$.[48] A unique feature of the last of these is that, being derived from coherent averaging theory, the phase of the overall rotation is also compensated (sequence of type A).

Figure 18 shows that 180° pulses can be created possessing compensation of simultaneous r.f. field and resonance offset imperfections. Two fairly short sequences with this property are $360_0 270_{180} 90_{90} 360_{270} 270_{90} 90_0$[42] and $360_0 180_{120} 180_{60} 180_{120}$.[47] The truly spectacular performance of Tycko's sequence of 25 180° pulses with phases[47]

0,0,120,60,120,0,0,120,60,120,120,120,240,180,240,60,60,180,120,180,120,120,240,180,240

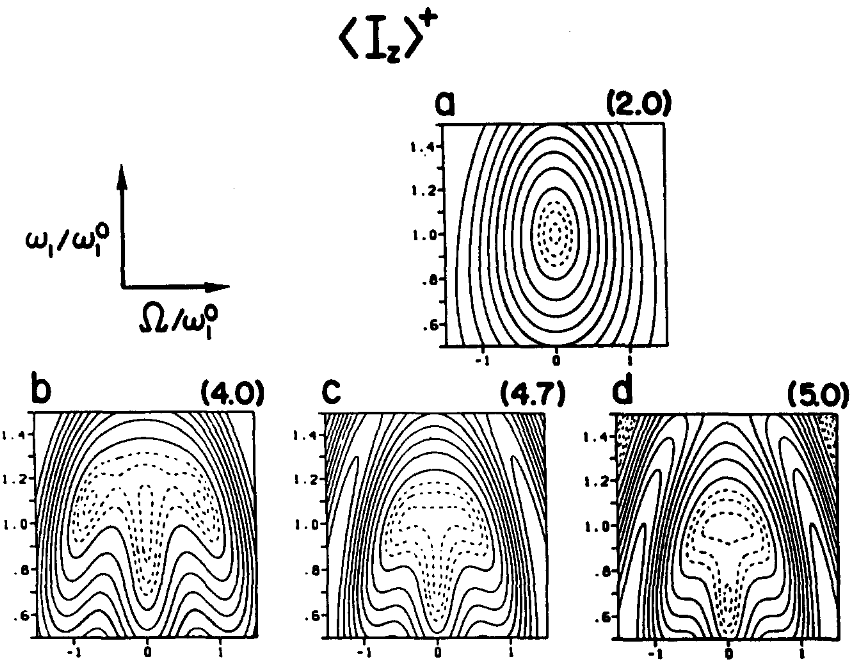

FIG. 15. Numerical evaluation of composite 180° pulses according to $\langle I_z \rangle^+$. (a) 180_0, (b) $90_{90}180_0 90_{90}$, (c) $90_{90}240_0 90_{90}$, (d) $90_{90}270_0 90_{90}$.[32-34]

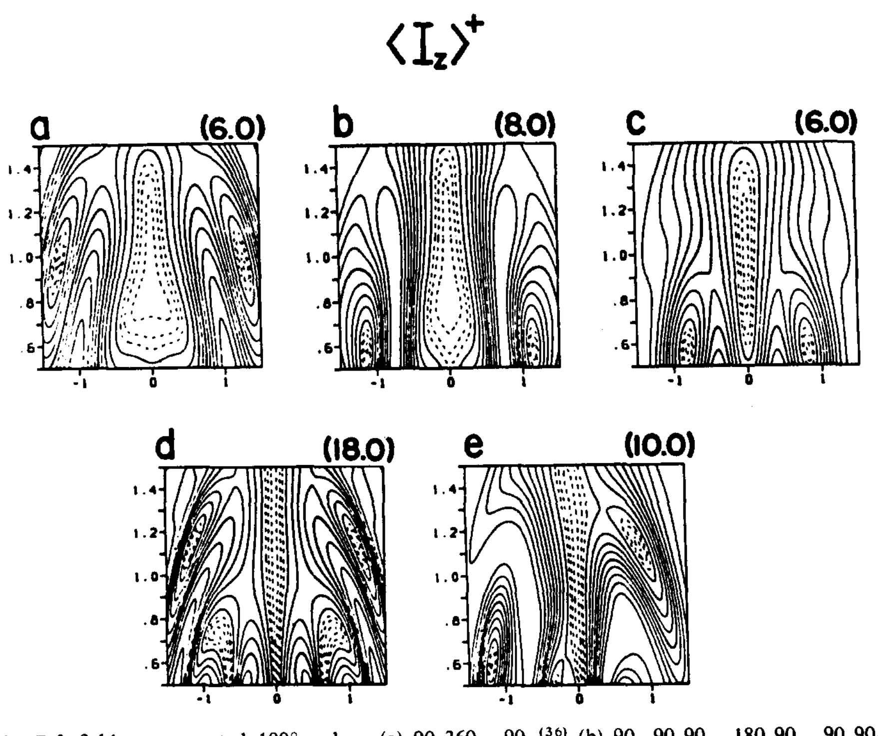

FIG. 16. R.f. field compensated 180° pulses. (a) $90_0 360_{120} 90_0$,[36] (b) $90_{90}90_0 90_{270}180_0 90_{270}90_0 90_{90}$,[37] (c) $180_0 180_{120} 180_0$,[44] (d) $180_0 180_{90} 180_0 180_{120} 180_{210} 180_{120} 180_0 180_{90} 180_0$,[43] (e) $180_0 180_{105} 180_{210} 360_{59}$.[48]

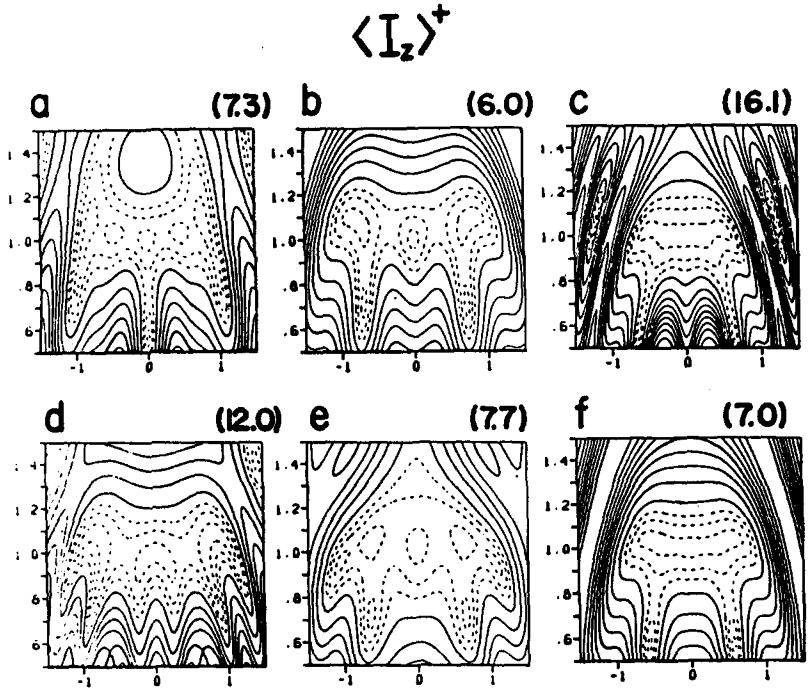

FIG. 17. Resonance offset compensated 180° pulses. (a) $90_0 200_{90} 80_{270} 200_{90} 90_0$,[36] (b) $90_0 180_{180} 270_0$,[20,21] (c) $336_0 246_{180} 10_{90} 74_{270} 10_{90} 246_{180} 336_0$,[48] (d) $180_0 360_{180} 180_0 270_{180} 90_0$,[20,21] (e) $39_{329} 54_{209} 66_{139} 84_{70} 267_0 84_{70} 66_{139} 54_{209} 39_{329}$,[24] (f) $90_0 225_{180} 315_0$.[50]

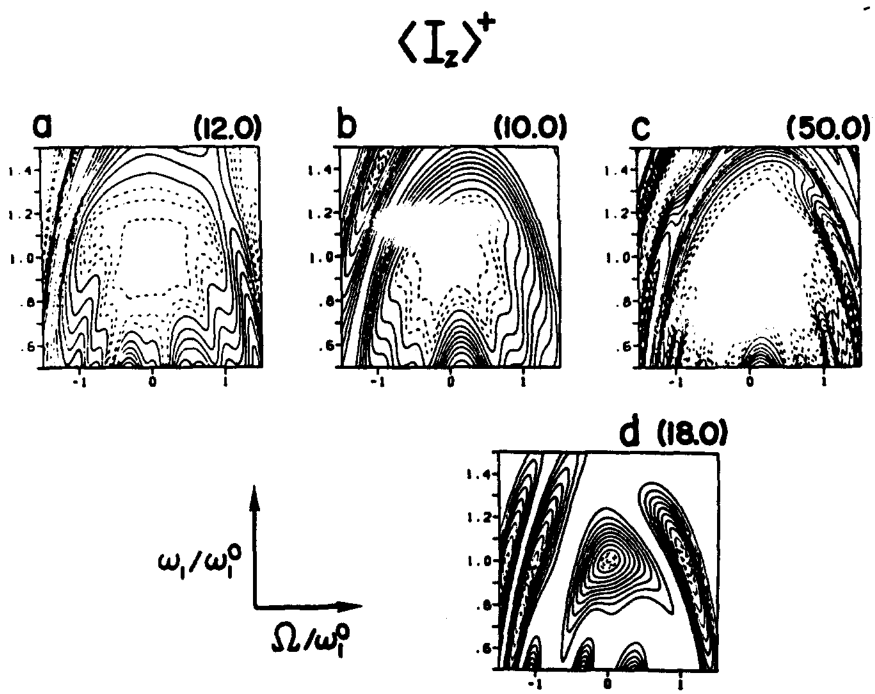

FIG. 18. Composite 180° pulses with simultaneous r.f. field and resonance offset compensation (a) $360_0 270_{180} 90_{90} 360_{270} 270_{90} 90_0$,[42] (b) $360_0 180_{120} 180_{60} 180_{120}$,[47] (c) Tycko 25-pulse sequence,[47] and the r.f. selective sequence (d) $180_0 180_{90} 180_{180} 180_{120} 180_{210} 180_{300} 180_{240} 180_{330} 180_{60}$.[43]

is also shown; it is unfortunate that this sequence is too long for gereral applications. Figure 18 also gives the performance of the sequence[43]

$$180_0 180_{90} 180_{180} 180_{120} 180_{210} 180_{300} 180_{240} 180_{330} 180_{60}$$

designed to give a good population only at a specific value of r.f. field, and to leave the spin system unperturbed at other values. From the plot given, it is clear that great care must be exercised in minimizing off-resonance effects if this sequence is to operate correctly.

4.3. *Usage*

The applications of a given composite pulse are determined by its category. Composite pulses of type A may be used in all contexts. However they do often involve inconvenient phases, and especially for off-resonance effects, a limited range of compensation. Composite pulses of categories B1, B2 and B3 may not always be used, since the precise form of the propagator depends on the pulse imperfections, but when they can, they will often be found to have advantages over those of category A.

4.3.1. *Pulses of type B2 and B3.* Pulses of categories B2 and B3 are the most limited in their use. Since they are only compensated for the conversion of I_z into a specific final condition, they are successful only for those experiments where this is the only transformation which occurs. This implies that they may be applied only in the case that the system is described by populations alone, coherences being absent. In addition, it must be decided if the phase of the final density operator is important. For example, when transverse magnetization is excited by a 90° pulse, offset-dependent phase errors are unimportant since they are easily corrected after Fourier transformation of the signal by complex multiplication of the data. Therefore in this context offset-compensated pulses of type B3 are sufficient, and often a single 90_0 pulse is good enough. On the other hand, if an inhomogeneous r.f. field is present and it is desired to excite a signal, phase errors proportional to the r.f. field strength may not be tolerated since they cause destructive interference between signals from different volume elements. In this case, no manipulations of the spectrum can retrieve the loss. Thus composite 90° pulses of class B2 (or A) are called for in exciting the signal in an inhomogeneous r.f. field.

Similar considerations apply to composite 180° pulses, although here it is almost always possible to use pulses of type B if care is taken. In contexts where the sign inversion of I_z is the necessary transformation, pulses of type B may clearly be used. Even in situations where the 180° pulses are used as refocussing pulses, phase errors in the rotation produced by composite pulses of type B can always be compensated by refocussing twice instead of once.[34] Alternatively, the whole pulse sequence, including the 90° pulses, etc. can be compensated in phase-consistent fashion by using throughout sequences of type A or B1 (see below).

4.3.2. *Pulses of type A and B1*; *supplementary z-rotations.* General pulse sequences in which the pulses operate on a wide variety of initial conditions must be compensated using sequences of type A or B1. This needs care when the composite pulses are such that they require "supplementary *z*-rotations" to put the propagators in the required form. For example the propagator of the r.f. field compensated 90° pulse[48] $270_{180} 360_{349} 180_{213} 180_{358}$ is equivalent to that of 90_0 only if supplemented with a final $[70_z]$ rotation. These *z*-rotations, which are independent of the imperfections, must be taken into account experimentally by changing the phase of *subsequent* pulses, in the *opposite* direction to the *z*-rotation as written. Thus the sequence $270_{180} 360_{349} 180_{213} 180_{358}$–$\tau$–$270_{180} 360_{349} 180_{213} 180_{358}$ does *not* behave like 90_0–τ–90_0, whilst the sequence $270_{180} 360_{349} 180_{213} 180_{358}$–$\tau$–$270_{110} 360_{279} 180_{133} 180_{288} [140_z]$ would. Not all sequences require a supplementary *z*-rotation; the 180° pulse $180_{225} 180_0 180_{105} 360_{314}$ does not, for example.

A similar situation arises if composite pulses of type B1 are chosen, for example for wideband compensation of off-resonance effects. When derived by the procedures given in Sections 3.3.–3.5, this leads to sequences with propagators of the form eqn. (82). Again each pulse is associated with a supplementary z-rotation. But this time the way the sequence is constructed implies that the supplementary z-rotation is equal in magnitude to the nominal flip angle, requiring a phase shift of all subsequent pulses by minus that amount. When *all* pulses are built up the same way, by juxtaposing sequences $(P_{\beta}^{(m)})^{\text{inv}}$ and $P_0^{(m)}$ as in Section 3.5, a simple procedure can be devised for specifying the phase of all pulses in the sequence: Replace all pulses $(\beta_p^0)_{\phi_p}$ by composite pulses $(P_{\phi'_p}^{(m)})^{\text{inv}}\ P_{\phi''_p}^{(m)}$, where the phases ϕ'_p and ϕ''_p used for the two halves of each composite pulse are given by

$$\phi'_p = \phi_p - \textstyle\sum_{q=1}^{p-1} \beta_q \tag{104}$$

and

$$\phi''_p = \phi'_p - \beta_p^0. \tag{105}$$

Equation (104) takes into account the intended phase ϕ_p of the rotation and the history of all accumulated z-rotations. Equation (105) supplies a phase difference between the two halves of the composite pulse which is equal to the intended rotation angle. A sequence compensated in this way has an overall propagator which differs from that for an ideal pulse sequence only by extra phase rotations of the initial and final conditions:

$$U_{\text{comp}} = \exp\{-i\textstyle\sum_k(\phi_k^{(m)} - \sum_{q=1}^{p}\beta_q^0)I_{kz}\}\,U^0\exp\{i\sum_k\phi_k^{(m)}I_{kz}\} \tag{106}$$

where $\phi_k^{(m)}$ are properties of the composite pulse, eqn. (82), and U here signifies the propagator for the entire pulse sequence including delays. Since the composite pulses are of type B1, the phase errors $\phi_k^{(m)}$ may be dependent on the imperfections. But especially in the case of off-resonance effects, these extra phase factors are easily corrected and should not present a problem.

To make this discussion concrete, consider the pulse sequence for double-quantum spectroscopy:

$$90_{\phi 1} - \tau/2 - 180_{\phi 2} - \tau/2 - 90_{\phi 3} - t - 90_{\phi 4} - t_2 \tag{107}$$

where the phases ϕ_1 to ϕ_4 may be cycled from transient to transient to achieve selection of a particular history of coherence orders,[79] but this does not concern us here. To compensate this sequence for large resonance offsets, it is neccessary to use composite pulses of type B1. Sequences of the form $(P_\beta)^{\text{inv}}\ P_0$ are suitable where $P_0 = 90_0$ and $(P_0)^{\text{inv}} = 180_{180}360_0 180_{180}270_0$ (Section 3.4). Employing eqns. (104) and (105), the compensated sequence is

$$\begin{aligned}
&180_{\phi 1+180}360_{\phi 1}180_{\phi 1+180}270_{\phi 1}90_{\phi 1+90} - \tau/2 -\\
&180_{\phi 2+90}360_{\phi 2+270}180_{\phi 2+90}270_{\phi 2+270}90_{\phi 2+90} - \tau/2 -\\
&180_{\phi 3+270}360_{\phi 3+90}180_{\phi 3+270}270_{\phi 3+90}90_{\phi 3+180} - t_1 -\\
&180_{\phi 4+180}360_{\phi 4}180_{\phi 4+180}270_{\phi 4}90_{\phi 4+90} - t_2.
\end{aligned} \tag{108}$$

The sequence above is a rather more consistently constructed version of a compensated double-quantum pulse sequence published earlier.[38] It should produce the same result as a normal pulse sequence, except for having broadband characteristics, and for giving a final spectrum possessing an easily corrected phase gradient. Experimental results using this sequence are shown in Section 5.

If it is wished to compensate the same sequence for r.f. field errors, the same procedure may be used with B1-type composite pulses such as $P_0 = 90_0 90_{90}$ and $(P_0)^{\text{inv}} = 90_{270}90_{180}$. This compensates the main body of the pulse sequence but in this case the compensation effect is counteracted by phase errors dependent on the r.f. field strength which may cause partial destructive interference.[48] It is better to use sequences of type A in this case leading for example to

$$\begin{aligned}
&270_{\phi 1+180}360_{\phi 1+349}180_{\phi 1+213}180_{\phi 1+358} - \tau/2 -\\
&180_{\phi 2+185}180_{\phi 2+290}180_{\phi 2+35}360_{\phi 2+234} - \tau/2 -\\
&270_{\phi 3+110}360_{\phi 3+279}180_{\phi 3+143}180_{\phi 3+288} - t_1 -\\
&270_{\phi 4+40}360_{\phi 4+219}180_{\phi 4+73}180_{\phi 4+218} - t_2.
\end{aligned} \tag{109}$$

Let us repeat again the considerations which must be taken into account in deciding which procedure to use for compensating some general pulse sequence. Sequences of type A may always be used, but sometimes with the sacrifice of some bandwidth. It is permissible to use sequences of type B2 or B3 only if the initial condition is entirely described by populations. To choose between these two classes it is neccessary to decide if phase errors in the final density operator are tolerable, which will depend on the experiment. In compensating more general experiments, in which the pulses are applied to density operators involving coherences, one must choose between pulses of type A or B1. It is permissible to use sequences of type B1 if the phase of the final density operator can be shown to be unimportant. This is usually the case with off-resonance effects because phase correction after Fourier transformation is possible. It is also possible for correction of inhomogeneous r.f. fields in the case of heteronuclear experiments, where the pulses on the channel *not* to be observed are compensated, since the signal observed on one channel must always be independent of overall phase shifts on a different frequency. However, for compensation of r.f. field errors in homonuclear systems, sequences of type A are superior, since they do not give a phase distribution of the final signal which is a function of the r.f. field strength.[48] Whenever a general sequence is compensated by using composite pulses of type A or B1, care must be taken to take account of supplementary z-rotations by introducing extra phase shifts. For sequences of type B1, a simple recipe to do this is available since the supplementary z-rotation produced by each composite pulse is equal to its flip angle.

Finally, we should point out that if composite pulses of type A are used, it is permissible to replace the pulses one at a time by composite pulses, and provide a continuously improving performance. But if composite pulses of type B1 are employed, because of their phase characteristics it is usually essential to replace all pulses simultaneously by composite pulses of similar structure; no intermediate stages are possible.

5. APPLICATIONS OF ERROR COMPENSATION

In this Section we discuss the application of composite pulses to several experiments in isotropic liquids. We discuss separately the manipulation of populations, the manipulation of Hamiltonians and the manipulation of coherences.

5.1. *Manipulation of Populations*

The manipulation of energy level populations by composite pulses has proved to be one of the most straightforward and successful applications. The first application of a composite pulse was the accurate inversion of spin populations by the $90_0 180_{90} 90_0$ sequence, in order to allow measurement of relaxation times by timing the null-crossing in the recovery from completely inverted to thermal equilibrium populations.[32] This particular application can certainly be criticized on the grounds that the null-point method is certainly a very weak measurement technique anyway, and that in fact any other single point on the curve will do, providing the initial populations after the (imperfect) inversion are known, and the recovery is truly exponential. Single-point determinations cannot compete with measurement of the full recovery curve in accuracy and can only be justified if measurement time is limited. Nevertheless population inversion by a composite pulse is useful in routine T_1 determinations, even if a full recovery curve is measured, since the more exact the spin inversion, the higher is the dynamic range, and the more accurate the value of T_1. Also, very exact population inversion allows a 2-parameter fit rather than a 3-parameter fit. One must anticipate that for the same reason composite pulses could be used profitably to obtain T_1-dependent NMR images,[80] especially since r.f. fields are often quite inhomogeneous in high-frequency imaging systems.

Destruction of populations by composite 90° pulses is also useful in certain other methods for measuring relaxation times, such as 'saturation-recovery'.[4]

Composite 90° pulses find further uses in relaxation time measurements in coupled spin systems where it is sometimes desirable to ensure that only the *total* Zeeman magnetization $\sum_k I_{kz}$ is measured and not multiple-spin terms like $2I_{kz}I_{k'z}$, etc. After an ideal 90° pulse, the multiple-spin terms should be completely converted into multiple-quantum coherences and should give no signal. If the pulse is non-ideal, however, antiphase contributions to the signal may result. A composite 90° pulse which takes z-operators very exactly into the xy plane is appropriate in this case. Bodenhausen *et al.*[81] have suggested using composite pulses to suppress longitudinal multiple-spin order in two-dimensional nuclear Overhauser spectroscopy, and Shaka *et al.*[71] have demonstrated the utility of composite pulses of type B3 (in particular, $360_0 270_{180} 90_{90}$), for a similar purpose in nuclear Overhauser difference spectroscopy. The very accurate and wideband destruction of z-magnetization by $360_0 270_{180} 90_{90}$ (Fig.14) makes it very well-suited for this particular purpose.

5.2. *Manipulation of Hamiltonians*

The most important application of composite pulses for the manipulation of spin Hamiltonians is of course broadband heteronuclear decoupling by such sequences as WALTZ-16.[11–23] However treatment of this large subject is beyond the scope of this article.

Another application which might be considered as a manipulation of a spin Hamiltonian is the refocussing of magnetic field inhomogeneity by multiple 180° pulses.[34] In the absence of spin–spin couplings, in which case special problems are encountered (see below), it was suggested that composite pulse schemes might be better for compensating cumulative pulse imperfections than the usual Meiboom–Gill method, which makes no attempt to compensate the individual rotations but simply places the magnetization vector in a favourable position with respect to the imperfections by introducing a 90° phase shift between the initial 90° pulse and the train of 180° pulses.[56] Composite pulses compensate the individual rotations themselves, and so so should be superior. (In this application, error-dependent phases of the B-type composite pulses may be compensated by using an even number of echoes.[34]) Actually this application of composite pulses proves disappointing on closer inspection. It turns out that in the Meiboom–Gill method, the major effect of the pulse imperfections is to 'lock' the transverse magnetization along its initial position, which tends to overcome interference from field fluctuations and other perturbations, and often actually *improves* the appearance of the multiple-echo train. The locking effect is reduced if the compensated pulses are introduced, so here the more highly-compensated sequence often behaves in an apparently *worse* manner. This 'double-edged' nature of pulse imperfections is a common feature of many experiments and has often made it harder than anticipated to demonstrate the benefits of composite pulses.

Another application of accurate broadband cycles which can be conceived is one where very dense pulse sequences are applied to coupled spin systems for long periods of time in order to create evolution under an effective Hamiltonian which contains scalar couplings but no chemical shift terms ('isotropic mixing').[82–84] If the correlations between coherences are mapped out using two-dimensional spectroscopy,[5,6] transfer of information between quite distant spins can be demonstrated. Almost any dense pulse sequence suppresses chemical shift interactions leaving scalar couplings, but only broadband cycles could do this without producing any other overall rotation of the spin system. There are cases where this might be useful, since the high symmetry of the pure isotropic coupling Hamiltonian is responsible for a large number of selection rules, leading to a considerable simplification of the two-dimensional spectrum.[62] Bax *et al.*[85] have also proposed a variant of this method in which alternating-phase spin-locking is applied for the mixing instead of a sequence of discrete π pulses. If composite pulses are interposed between the periods of opposite phase irradiation, this variant is less sensitive to off-resonance effects. The compensated mixing sequence which has been suggested is $(\beta_0\ 300_{180}\ 60_0\ \beta_{180}\ 300_0\ 60_{180})^n$, where β is large and n is a small integer.

5.3. *Manipulations of Coherences*

Composite pulses are definitely useful in improving the accuracy of coherence transfer processes.

They are especially important if a pulse occurs in the middle of the evolution period in a two-dimensional experiment, so that the frequencies in the spectrum should be linear combinations of the evolution frequencies of particular pairs of coherences before and after the pulse. This is the case in two-dimensional J-spectroscopy,[86] where a 180° pulse occurs in the middle of the evolution period to transfer the accumulated phase of one coherence to another related by spin inversion [eqn.(16)]. It is also true in heteronuclear two-dimensional experiments, where a centrally-placed 180° pulse on one spin species is used for removing heteronuclear coupling frequencies in the ω_1-dimension.[87] 180° pulses are also often used in multiple-quantum spectroscopy,[1,2] to refocus magnet inhomogeneity, and in two-dimensional nuclear Overhauser spectroscopy,[88,89] where they are introduced with variable timing so as to shift the frequencies of zero-quantum interference peaks.[90,91] In all these experiments, it is important that the 180° pulse induces only the desirable coherence transfers, otherwise unwanted lines appear in the two-dimensional spectrum. The suppression of such artefacts by composite pulses has been demonstrated,[92] and their consistent use can be recommended. However it is wise to remember that strong coupling, like pulse imperfections, can also cause an unwanted mixing of coherences, so that not all unwanted spectral lines can always be removed by introducing composite pulses. In the case of heteronuclear correlation spectroscopy, it is therefore better to use full broadband decoupling by a sequence like WALTZ-16 rather that to introduce a central 180° (composite) pulse to produce decoupled frequencies in the ω_1-dimension.[93]

Measurement of spin-spin relaxation times in coupled spin systems by multiple-echo trains also requires accurate 180° pulses to avoid loss of control over the coherences. Advantages in using composite 180° pulses could be demonstrated.[34] However it must be pointed out again that only in very weakly-coupled 'model' systems can successive coherence transfers be carried out accurately enough, and even in favourable cases the 180° pulses must be very widely separated. If closely-spaced 180° pulses are used, coherent averaging theory may be used to derive an effective Hamiltonian which is independent of the precise rotation angles,[10] so it is more or less irrelevant if composite pulses are used in this limit anyway. The intermediate regime with pulses spaced by durations comparable to the inverse of the chemical shift differences produces very complicated dynamics which are not very informative. All in all, spin–spin relaxation time measurements do not turn out to be a very favourable field for exploiting composite pulses.

Composite pulses are useful in overcoming problems of resonance offset and r.f. inhomogeneity in experiments designed to excite multiple-quantum coherence or multiple-spin order, such as homonuclear and heteronuclear polarization transfer and multiple-quantum filtering methods. In these techniques the density operator is passed through a series of unitary transformations designed to drive it into a specific form, and the effect of pulse imperfections is usually cumulative. For example, in double-quantum filtering of carbon-13 spectra in order to detect selectively low-abundance ^{13}C–^{13}C pairs ('INADEQUATE'[94]), the desired signal in the usual method may be shown to be roughly proportional to $\{1-5(\Omega/\omega_1^0)^2\}$, where it is assumed for simplicity that the two spins have almost equal offsets Ω. In practice, an r.f. field $\omega_1^0/2\pi \simeq 12.5$ kHz might be available (corresponding to a 90° pulse length of 20μs), so a loss of about half the signal may be predicted for ^{13}C resonances separated by only 8 kHz in resonance frequency, or 100 ppm at 80 MHz, a not uncommon situation. Such a strong offset-dependence is indeed observed.[38] The loss in signal is in general even more serious for experiments involving higher-order coherences or more pulses.

Experiments like these can be compensated in general only by using composite pulses of type A or B1, incorporated into the pulse sequence in a careful and consistent way such as to take into account of supplementary z-rotations, as has been described in Section 4.3. The performance of an INADEQUATE sequence incorporating composite pulses of type B1, eqn.(109), is compared with that of the uncompensated pulse sequence in Fig.19, for the natural abundance ^{13}C–^{13}C satellite spectrum of crotonaldehyde, which extends over almost 180 ppm. The 90° pulse length was 18μsec, an experimentally more realistic value than that used in Ref.(38). The off-resonance compensation is obvious from the observed spectral intensitites, enhancements of factors of three being observed for some satellites. It is interesting to observe that a noticeable enhancement in intensity was observed even when both participating spins were quite close to the carrier; One can therefore honestly recommend this pulse sequence to be used routinely. (The main peak signals were poorly suppressed

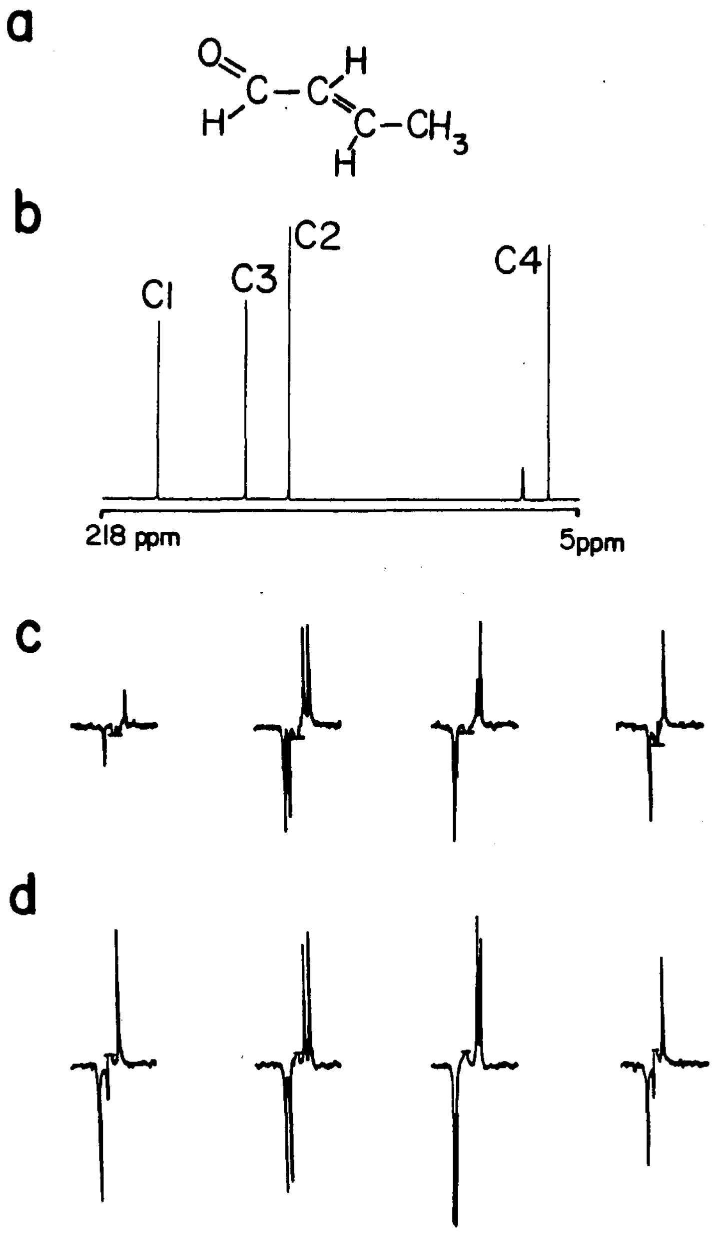

FIG. 19. Double-quantum filtered ^{13}C–^{13}C satellite spectra (INADEQUATE spectra) obtained at 75MHz on a modified Bruker CXP-300 spectrometer. (a) Crotonaldehyde, (b) conventional ^{13}C spectrum (one transient), (c) and (d) expanded ^{13}C–^{13}C satellite regions filtered through (± 2)-quantum coherence [94], without and with compensation for resonance offset effects during the pulses (1024 transients). The main peak signals were poorly suppressed in both cases for unknown reasons and have been deleted from the spectra shown for the sake of clarity. For (d) the composite pulse sequence of eqn.(108) with $t_1 = 0$ was used. The r.f. field strength was $\omega_1/2\pi = 13.2$ kHz. There is a clear enhancement of the satellite signals in (d) which is due to offset compensation.

in both non-compensated and compensated spectra and have been whited out in the plots shown; the poor suppression seems to derive from an unidentified stability problem on our instrument and is not relevant to the compensation issue.)

6. PRACTICAL IMPLEMENTATION

In this Section we discuss how to implement composite pulses in practice, assuming there is an instrument available equipped with a versatile pulse programmer and an accurate (preferably digital) phase shifter.

Composite pulses may normally be implemented in the pulse programme by simply chaining together instructions for pulses of different phase. Experience has shown that it is *not* necessary to leave a delay between the pulses to let the phases 'settle'. Transients will occur anyway whether or not this is done, and inter-pulse delays will degrade the performance at large resonance offsets. However it is usually recommended to preset the phase of the carrier to the phase of the first element in the composite pulse before the transmitter gate is turned on, and to hold the phase to that of the last element for a few μsec after the pulse is turned off. This is especially important if phase-cycling is done to select particular coherence transfer pathways.[79] Phase presetting ensures that if the pulse sequence is shifted in phase, the overall propagator is simply rotated around the z-axis, *including* minor transient effects at the beginning and end of the pulse. (This recommendation is valid whether or not composite pulses are used.) The suppression of unwanted pathways is improved by this means.

Especially when phase cycling is used, it is highly convenient, but not essential, to be able to place the composite pulses in a subroutine to which an overall phase can be passed. All the 'internal' phases of the composite pulse can then be calculated with respect to this overall phase. In addition, when using composite pulses with supplementary z-rotations, the subroutine can keep track of the accumulating phase rotations making explicit calculation on the lines of eqns.(104),(105) unneccessary. The pulse programming software available at the ETH in Zürich allows such facilities. It incorporates a small compiler written in ASPECT-2000 assembler code and runs on a modified Bruker CXP-300 spectrometer equipped with a commercial (Interface Technology RSM-232) pulse programmer and home-built 15° digital phase shifters. Pulse programmes are written in a custom-built high-level language with similar appearance to the current Varian system, but are more versatile and are compiled in less than a second. The pulse programmer hardware itself is not intelligent but fast enough to execute complicated multiple-pulse cycles such as are common in solids.

It is strongly recommended that an oscilloscope, coupled into the transmitter output, is available for examining the pulse sequences by eye, since some pulse programming systems may introduce hidden delays, or get confused when many short pulses follow each other in rapid succession. It is usually possible to check the timing of the phase shifts within a composite pulse by the the brief 'spikes' in reflected power.

It is usually best to verify at first the performance of composite pulses in a very simple application. For example, a composite 180° pulse can be checked by measuring the degree of inversion of equilibrium z-magnetization. The intensity of the signal is measured after a second 90° 'read' pulse which need not be composite. At least two scans should be combined, the second having the composite pulse shifted in phase by 180° to remove signals deriving from stray single-quantum coherence produced by the composite pulse. (This is much more reliable than attempting to defocus the transverse magnetization by applying a static field gradient.) A composite 180° pulse should give a distinctly higher intensity of inverted signal than a single 180° pulse. If this is not the case then the pulse programmer timing or phase shifts may be suspected.

The tempting 'short-cut' of assessing a composite 180° pulse by measuring the 'direct' signal it creates when applied to thermal equilibrium magnetization is potentially ambiguous and should be avoided. One often finds in fact that the composite 180° pulse gives larger residual signals than a single 180° pulse. This does not indicate that the composite pulse does not work but is an illusory effect deriving from destructive interference. In an inhomogeneous r.f. field, the signal is a sum of contributions form different parts of the sample. Composite 180° pulses should lead to smaller intensities of the individual signal components than a single pulse, but the overall signal also depends on the relative phases of the signal components. For a single 180_0 pulse, applied on-resonance, the y-magnetization is given to first-order in $\delta\omega_1$ by

$$\langle I_y \rangle^+ \simeq -(\pi \delta\omega_1/\omega_1^0). \tag{110}$$

If the r.f. field distribution is symmetrical around ω_1^0, the net signal is zero (this assumes a perfectly homogeneous static field B_0, otherwise the r.f. inhomogeneity can be partially refocussed during the formation of the free induction decay; but even in this case, the integral of the spectral line is zero). On the other hand, if a composite pulse $90_{90}180_0 90_{90}$ is applied to z-magnetization, the transverse magnetization is given to second order by

$$\langle I_y \rangle^+ \simeq -\tfrac{1}{2}(\pi \delta\omega_1/\omega_1^0)^2. \tag{111}$$

The transverse magnetization always has the same sign, so when averaged over a r.f. field distribution the composite pulse may give a larger net signal than a single pulse. But this is only the result of fortuitous destructive interference when using the single pulse, and the effect is usually absent in an actual experiment.

Similar effects exist for composite 90° pulses in inhomogeneous r.f. fields. Thus the *net* z-magnetization produced by a single 90° pulse can be set to zero by suitable choice of the pulse duration, whilst that produced by $90_0 90_{90}$ cannot, although the latter gives smaller individual contributions. Again, one must decide if such destructive interference effects are present in the actual experiment which is to be performed.

The more complicated procedures of type A or B1 are also best tried out on some simple application first, especially to test if the supplementary z-rotations have been correctly taken into account. Of course for these sequences an intelligent pulse programming software system is a great asset, and may make the implementation almost invisible.

7. UNORTHODOX APPLICATIONS

It has recently been recognized that the concept of applying a series of non-commuting rotations to the spin system has applications reaching beyond the compensation of pulse imperfections. Two of the 'unorthodox' applications which have been proposed involve not fighting against inhomogeneous r.f. fields, but using them in the one case to obtain spatial selectivity of NMR responses, and in the other case to cause a destructive phase dispersal of unwanted signals whilst leaving desired signals coherent. Another 'unorthodox' application is to extend the concept of compensating rotations to evolution under Hamiltonians non-linear in the spin angular momentum operators. All of these applications are still under development and not much detail will be given here.

7.1. *Radio-Frequency Field Selection*

The development of surface coils for detection of NMR signals inside large, intact objects, such as living subjects, has led to problems of achieving spatial selectivity of the NMR responses. Spatial selectivity may be achieved by applying static field gradients and frequency-selective r.f. pulses,[95] but an attractive, 'mobile' solution would be to use the spatial variation of r.f. field produced by the surface coil itself to select the desired volume. This requires a method of selectively exciting spins experiencing a particular value of r.f. field, and would ideally be insensitive to the precise resonance frequency of those spins. Bendall *et al.*[96] suggested a method involving phase cycling a series of 180° pulses to cut out signals experiencing unwanted r.f. fields. The problem with this method is that each individual 180° pulse has only a poor selectivity, so that many 180° pulses must be used, which must be cycled independently, requiring many experiments. Shaka *et al.*[43,97,98] and Tycko *et al.*[46] independently suggested using composite 180° pulses which have an intrinsic r.f. field selectivity. This cuts down greatly the number of experiments which must be combined.

Increasing the r.f. field selectivity of a pulse sequence is the exact opposite of r.f. field compensation and has been termed 'retrograde' compensation.[43] The ideal retrograde compensated 180° pulse produces a spin inversion only for $\omega_1 \simeq \omega_1^0$ and produces a rotation around the z-axis for other r.f. field values. Just as for compensated 180° pulses, iterative expansion procedures can be developed to generate retrograde compensated pulses. The above authors both suggested the retrograde compensation expansion

$$R_0^{(m+1)} = R_{-\phi}^{(m)} R_0^{(m)} R_{\phi}^{(m)} \tag{112}$$

where $\phi = 120°$. Shaka *et al.*[43] also showed that the same procedure with $\phi = 90°$ is useful for obtaining an initial 'coarse' retrograde compensation which can then be followed up with a 'fine' adjustment by using $\phi = 120°$. They recommended the sequence[43]

$$180_0 180_{90} 180_{180} 180_{120} 180_{210} 180_{300} 180_{240} 180_{330} 180_{60}. \tag{113}$$

Consulting Fig.18, this sequence does indeed give good r.f. selectivity close to resonance. But it is clear that it is highly offset-sensitive. Some suggestions for reducing this problem have been made, by combining different experiments,[97] and this aspect is undergoing further development.

7.2. *Composite* z-*Pulses*

Rotations of the spin density operator by an angle β^0 about the z-axis can be achieved by a composite pulse sequence $90_{270}(\beta^0)_0 90_{90}$, where all pulses are assumed ideal.[35] For instruments equipped with phase shifts only in steps of 90°, this proves an attractive way to simulate other phases, since a rotation of the spin density operator through β^0 about the z-axis is equivalent to a shift in the phase of the reference frame through $-\beta^0$. Thus the effect of an arbitrary phase shift can be mimicked simply by applying a sequence of pulses with orthogonal phases. Applications to various experiments in multiple-quantum spectroscopy have been reported.[99,100]

The advent of versatile and accurate digital phase shifters has caused this application to decrease in importance, since the rotation produced by a z-pulse is dependent on ideal pulse performance, whilst a digital phase shifter may be constructed to be almost arbitrarily precise. If necessary, the outer 90° pulses may be compensated (using sequences of type A or B2), but there is no apparent way to compensate the central $(\beta^0)_0$ pulse. However this sensitivity of the central pulse to effects such as r.f. inhomogeneity may be turned to advantage as follows. Suppose the r.f. field is only slightly inhomogenous, so that the outer 90° pulses may be considered ideal, whilst the central pulse is deliberately made long so as to amplify the effect of the small r.f. field variations. Then the sandwich $90_{270}(\beta^0)_0 90_{90}$ implements an *inhomogeneous z-rotation*, in which volume elements in different r.f. fields are rotated about the z-axis through different angles. If the duration of the central pulse is made long compared to the inverse of the spread in r.f. fields, an inhomogeneous z-rotation is generated with a rotation angle so strongly spatially-dependent as to be pseudo-random.

Such a long z-pulse is clearly useless for simulating r.f. phase shifts. However it produces a similar effect to a static field gradient pulse, except that it does not disturb the field-frequency lock or produce eddy currents in shim coils or probe housing (although other effects such as sample heating may be produced). Therefore long composite z-pulses may be used to select coherences according to their order.[41] Suppose two long z-pulses are applied, of unequal durations τ and $\kappa\tau$, on either side of some pulse sequence which mixes coherences of different orders. A coherence $|r\rangle\langle s|$ of order $p^{(rs)}$ accumulates a phase factor $\exp(-ip^{(rs)}\omega_1(\mathbf{r})\tau))$ during the first inhomogeneous z-pulse, where $\omega_1(\mathbf{r})$ is the spatially-dependent r.f. field. For a sufficiently long z-pulse, the coherence defocusses completely. Now suppose the coherence $|r\rangle\langle s|$ is transferred to a different coherence $|m\rangle\langle n|$ by the mixing sequence, and the second inhomogeneous z-pulse applied. The accumulated phase factor for the pathway $|r\rangle\langle s|\rightarrow|m\rangle\langle n|$ is $\exp\{-i(p^{(rs)}+\kappa p^{(mn)})\omega_1(\mathbf{r})\tau\}$. Contributions to the signal taking this pathway are spatially defocussed in phase unless $p^{(rs)}=-\kappa p^{(mn)}$. If this condition is satisfied, the defocussing is exactly reversed and the pathway is spatially coherent. In this case a 'rotary coherence transfer echo'[(41)] is formed, which represents a way of selecting signal components on the basis of their history of coherence orders, just as in phase cycling, with the difference that ideally only one experiment has to be performed. Thus the time requirements of various experiments can be reduced, or alternatively, the method can be combined with phase cycling to yield high suppression ratios of unwanted signals.

Some experimental results are shown in Fig.20, for double-quantum filtering of spectra from a mixture of A_2 and AX spin systems. Details are given in the caption. The technique basically works, although an undesirable reduction in the intensity of the AX peaks is produced, since only one of either (+2) or (−2)-quantum coherences can be refocussed simultaneously, whilst in selection of double-quantum coherence by phase-cycling, both may be retained. Nevertheless the method may be useful in cases where experimental time would be excessive if full phase-cycling were employed, and signal-to-noise ratio is sufficient.

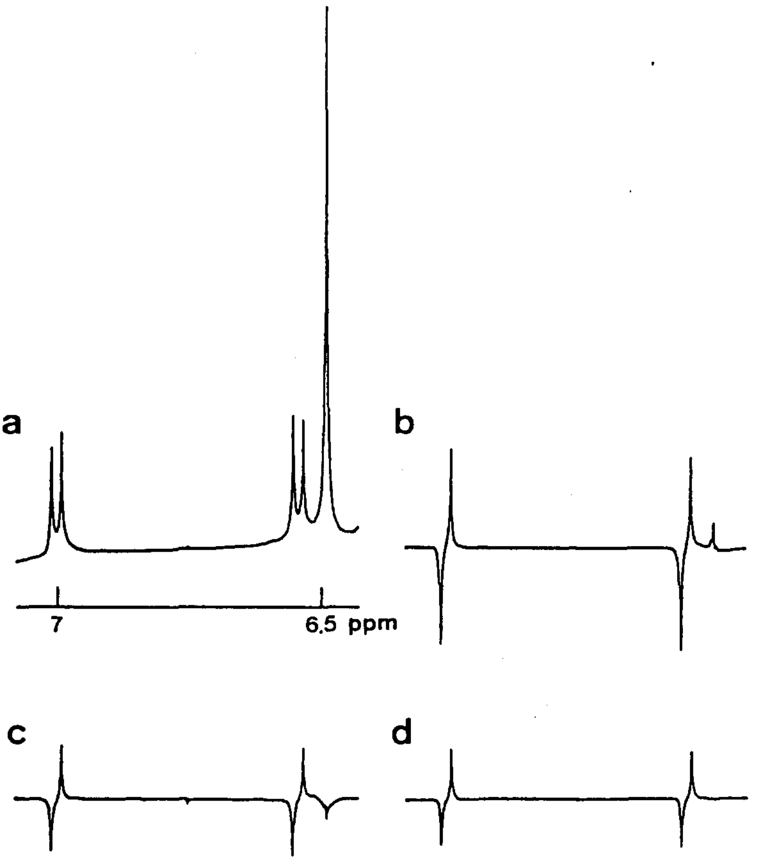

FIG. 20. Use of inhomogeneous z-pulses for selection of coherence orders. Spectra are of a mixture of proton A_2 and AX spin systems, and are scaled to correct for the fact that they were taken with a different number of transients. (a) Conventional spectrum (one transient) (b) Spectrum obtained by (±2)-quantum excitation, selection of (±2)-quantum coherences by a 4-step phase cycle, and excitation of observable magnetization with a 90° pulse (4 transients). (c) Spectrum obtained by (±2)-quantum excitation, an inhomogeneous z-pulse of duration 200μsec, a 90° pulse, and an inhomogenous z-pulse of duration 400μsec (one transient). The pair of z-pulses filter out (+2)-quantum coherences. (d) Combination of phase cycling and inhomogeneous z-pulses (4 transients). (From Ref. 41.)

The implementation of unorthodox rotations by composite pulses is not restricted to rotations about the z-axis. For example, Caravatti *et al.*[101] have described sequences such as $35.3_{135}120_{45}35.3_{315}$ to induce rotations of the spin system through 120° about the tetrahedral axis (1,1,1), with applications in solid-state heteronuclear correlation spectroscopy; It is worth pointing out that the somewhat simpler sequence $90_{90}90_{0}$ produces the same rotation.

7.3. *Composite Bilinear Rotations*

By applying pulse sequences which are long enough for spin–spin couplings to operate, it is often possible to cause the density operator to evolve under an effective Hamiltonian which is bilinear in the spin angular momentum operators. For example the effective Hamiltonian $H_{eff} = \sum_{k,k'} 2\pi J_{kk'} I_{ky} I_{k'y}$, may be produced by applying a pulse sequence 90_0–$\tau/2$–180_0–$\tau/2$–90_0 to a weakly-coupled spin system. Such evolution operators are often referred to as 'bilinear rotations'. They have been shown to be useful concepts in many experiments such as decoupling,[102] multiple-quantum NMR,[103] and various forms of two-dimensional correlation spectroscopy.[62,104,105] A particular useful bilinear rotation is used in experiments on dilute heteronuclear spin systems, where the following pulse sequence on abundant spins I and dilute spins S leads to evolution under the effective Hamiltonian $H_{eff} = \sum_k \pi J_k 2I_{ky}S_z$, where J_k are heteronuclear couplings between the S spin and the neighbouring I-spins:

$$\begin{array}{ll} I: & 90_0\text{–}\tau/2\text{–}180_0\text{–}\tau/2\text{–}90_0 \\ S: & \qquad\quad 180_0. \end{array} \tag{114}$$

(An additional 180° rotation of the S-spins also results, but this is usually immaterial.) Because there is a large difference in the magnitude of one-bond IS scalar couplings and longer-range couplings, this sequence allows selective manipulation of I-spins directly bonded to an S-spin, and has been put to a large number of ingenious purposes.[102,104–108]

Difficulties with the bilinear rotation arise if the duration τ of the sequence is not matched to the one-bond couplings J_k. (Usually, τ should be $1/J_k$). This might be impossible to achieve if there is a range of one-bond couplings, and leads to a sort of 'inhomogeneity' in the bilinear rotations, the 'inhomogeneity' in this case not being spatial but from spin system to spin system. Similar methods as used to correct r.f. field variations in ordinary pulses can sometimes be extended to the bilinear case. For example, Garbow *et al.*[102] suggested the sequence

$$\begin{array}{ll} I: & 90_0\text{–}\tau/2\text{–}180_{90}\text{–}\tau/2\text{–}90_{270}\text{–}\tau\text{–}180_{90}\text{–}\tau\text{–}90_{90}\text{–}\tau/2\text{–}180_{90}\text{–}\tau/2\text{–}90_0 \\ S: & \qquad\quad 180_0 \qquad\qquad\qquad\quad 180_0 \qquad\qquad\qquad 180_0 \end{array} \tag{115}$$

which provides a bilinear rotation $\exp\{-i\pi\sum_k 2I_{kx}S_z\}$ relatively insensitive to variations in the coupling constants, by analogy with the composite pulse $90_0 180_{90} 90_0$. Wimperis *et al.*[108] have taken these compensation schemes further and developed bilinear rotation equivalents of the $1\bar{2}1$ and $1\bar{3}3\bar{1}$ 'solvent suppression' sequences,[52–54,109,110] as well as bilinear selective excitation sequences which produce appreciable signal only for I-spins directly bonded to an S-spin.[106–108]

Despite these fair successes, analogies between bilinear rotations and normal rotations must be drawn with care. In general the evolution of many-spin systems over periods long compared to the couplings occurs in spaces of much higher dimension than the three-dimensional spaces assumed for composite pulses and selective excitation sequences. In the heteronuclear examples given above, the analogies work fairly well because the large magnitude of one-bond IS couplings allows the much weaker II couplings to be ignored so that the evolution of the system may be restricted to a set of independent three-dimensional spaces $\{2I_{kx}S_z, 2I_{ky}S_z, I_{kz}\}$ for each spin I_k. In homonuclear spin systems, this simplification is not feasible, and compensated bilinear rotations cannot be created by known methods.

The compensated multiple-quantum rotations suggested recently by Barbara *et al.*[111] are closely related to compensated bilinear rotations but as they seem most likely to be applicable to the NMR of spins $I = 1$, they will be discussed in the following Section. In addition we should mention J-cross polarization sequences which may also be compensated for coupling variations by forming analogies with conventional composite pulses.[127]

7.4. *Virtual Composite Pulses*

Sometimes composite pulses are useful in thinking about the way an experiment works as well as for improving its performance. This is often the case when a sequence contains a pulse with a nominal rotation angle not equal to 90° or 180°. It is frequently enlightening to consider such a pulse, for example $(\beta^0)_{90}$, as a 'virtual composite pulse' such as $90_0[(\beta^0)_z]90_{180}$. When the sequence is looked at this way its operation may become easier to visualize. A good example is the DEPT sequence for polarization transfer from I-spins to S-spins.[112] The usual pulse sequence involves a $(\beta^0)_{90}$ pulse applied to the I-spins; the particular functional dependencies of the transferred polarization on the flip angle of this pulse depend on the type of spin system and can be used to achieve 'subspectral editing' of IS, I_2S and I_3S systems. However this is a purely mathematical argument and yields little physical insight. It is more revealing to substitute for the $(\beta^0)_{90}$ pulse a virtual composite pulse. It is then found [103] that the first 90° pulse of the sandwich creates multiple-quantum coherence amongst the I-spins, of orders (± 1) for IS systems, (± 2) for I_2S systems, and both (± 1) and (± 3) for I_3S systems. The variation of the pulse flip angle in the usual DEPT technique corresponds to a variation of the $[(\beta^0)_z]$ rotation, i.e. phase cycling in the usual way to distinguish between the different orders of I spin coherence created in the different spin systems. The final 90° pulse in the sandwich transfers this multiple-quantum coherence (partially) into observable S-spin magnetization. The functional dependencies are fully explained and it is seen how this pulse sequence relates to other techniques such as multiple-quantum filtered spectroscopy.[94] It is also apparent that non-idealities may cause "breakthrough" of systems with a larger number of I-spins into the subspectra of those with a smaller number, but not the other way around, since multiple-quantum orders of magnitude p can only be sustained in systems of larger than, or equal to, p spins-1/2.

In fact it usually turns out of advantage to actually do the experiment this way as well as just think about it.[38,113] The experiment is then closely related to compensation schemes involving sequences of type B1 discussed above, and displays reduced sensitivity to pulse errors. Of course the expansion of a pulse into a sequence of two pulses sandwiching a phase shift is the basis of the construction of many composite pulses as discussed in Section 3.

7.5. *Composite Pulses in other Spectroscopies*

Composite pulses may also be used in other forms of coherent spectroscopy providing the technology exists for producing pulses of controllable relative phases, and assuming that relaxation times are not prohibitively short. A natural candidate is pulsed electron spin resonance, where the problem of large spectral widths compared to currently available pulsed microwave intensities exists. Unfortunately if the width of the spectrum is caused in this case by hyperfine couplings or g-tensor anisotropies, no composite pulse is yet known for improving the bandwidth of the excitation; the problem is analogous to increasing the bandwidth of a single 90° pulse in a single nuclear spin-1/2 system, which has not been achieved beyond the rough limit $\Omega \simeq \omega_1^0$. But it might be possible to enhance excitation bandwidths for the pulsed ESR of triplet states, where the spin dynamics are similar to spins $I = 1$. No applications have been reported however, to the knowledge of the author.

Composite pulse techniques may be transferred in some cases to coherent optical spectroscopy.[74–76] This has been made possible by the recent introduction of acousto-optic modulation technology for the generation of phase-shifted coherent laser pulses.[74] The method involves deflection of a laser beam by an r.f. acoustic wave induced in a suitable crystal; the phase information of the r.f. pulses is transferred completely to the diffracted optical beam. Of course coherent optical spectroscopy encounters quite different problems form NMR so the interesting pulse sequences are also different. In optical systems one is usually in a situation of 'extreme inhomogeneous broadening' in which the linewidths are much larger than the electric–dipole–laser interaction. These very broad lines cannot be excited uniformly, as is a realistic goal in NMR and one often hopes to maximize instead the integrated excitation over the line, without concerning oneself with the detailed structure within the line. Warren has investigated closely the properties of phase-modulated sequences such as $(\beta_0\beta_{180})^n$, where n is large, and predicted by computer simulation an enhancement of the population inversion in a 2-level system,[76] which could also be verified experimentally. A similar effect was predicted in enhancement of the population inversion across the forbidden transition in optical 3-level systems.[76]

At present the application of composite pulses, and shaped pulses, in coherent optics is still somewhat restricted in real applications by the power-handling capabilities of the acousto-optic modulation devices. Technological innovations in this area are to be expected.

8. COMPOSITE PULSES IN SOLIDS AND LIQUID CRYSTALS

NMR in anisotropic media encounters special problems. The spectra are dominated by large anisotropic interactions such as chemical shifts, quadrupolar splittings (for $I \geqslant 1$) and dipolar spin–spin couplings.[114] The considerable size of these terms relative to the strength of the interaction of the spins with feasible r.f. fields is the principle cause of imperfect pulse performance. In this Section we discuss how composite pulses can help overcome this problem in favourable cases.

In high magnetic field all interactions may be factored into a spatial part multiplied by a spin part. Heteronuclear dipolar couplings and anisotropic chemical shift terms transform in the spin part as first-rank tensors (vectors), so that in cases where other interactions may be ignored, the techniques described in the earlier Sections may be applied. Offset-compensated composite pulses of types A, B1, B2 and B3 may all be used in the usual way.

We are more concerned here with cases where the dominant interactions transform in the spin part as second-rank tensors, and the first-rank terms like chemical-shift or heteronuclear coupling terms may be ignored over the duration of the pulse. When second-rank dipolar spin–spin couplings or quadrupolar interactions are the predominant cause of imperfect pulse performance, the theory developed above for vector interactions is inapplicable, and different sorts of composite pulse must be found.

There seem to be two distinct approaches to this problem. The first method is the most general. It sets out with the ambitious goal of compensating the effect of spectral broadening during the pulse, using only the fact that the interactions are second-rank in the spin variables, and not using any other knowledge of the system, such as the number of energy levels, etc. The second method, on the other hand, concentrates on one particular type of system, in the cases to be discussed a three-level system with unequal spacing, such as is found for spins $I = 1$ in an anisotropic environment or for isolated pairs of dipolar-coupled spins-1/2. The only parameter which is left free is then the size of the quadrupolar or dipolar interaction. The advantage of the first method is that, if successful, it would allow construction of composite pulses which may be used in a wide variety of systems. The second method is based on the expectation that by using as much information as possible, more compact and effective composite pulses can be built up.

8.1. *Coherent Averaging Method*

Coherent averaging theory is a suitable framework for designing a composite pulse based only on the second-rank transformation properties of the spin interactions and without any other assumption. The theory is the same as in Section 3.2. with the difference that the perturbation H_{small} is proportional to T_{20}, the M = 0 component of a second-rank tensor.[45] Upon rotations, T_{20} mixes with the four other second-rank tensor components $T_{2\pm1}$ and $T_{2\pm2}$, with mixing coefficients given by the elements of the appropriate Wigner rotation matrix. The task of designing a composite pulse reduces to finding a set of rotations which are equivalent to the chosen ideal rotation, and such that the time average of the Wigner matrix elements in the interaction frame vanishes, $\bar{H}^{(0)} = 0$.

The problem is closely related to disigning a multiple-pulse dipolar line-narrowing sequence,[10] where $\bar{H}^{(0)}$ for second-rank interactions should also be zero. However the ideal rotation in that case is also usually zero (the sequence is cyclic) and there is an additional constraint, that the time-average of the interaction frame first-rank interactions does not vanish (finite 'scaling factor'). Many sequences with this property have been proposed,[9,10] but the ones of most relevance here are the 'windowless' cycles of Burum *et al.*[115] ('windowless' means no gaps between the pulses). Burum *et al.* showed that the time-average of interaction-frame second-rank tensors vanishes for particular sequences of six 90° pulses, amongst others

$$90_0 180_{90} 90_{180} 180_{90} \tag{116}$$

The ideal propagator for this sequence is 180_0, so this sequence already represents a composite 180° pulse compensated to zeroth-order for second-rank interactions. Burum *et al.*[115] did not realize this possible application, however, and proceeded instead by "symmetrizing" the sequence (placing it next to its inverse, as defined in Section 3.4), and using the whole thing (now a cycle, called BLEW-12) for line-narrowing purposes.

Tycko *et al.*[45] have recognized the potential of such sequences for broadband population inversion in systems with second-rank interactions. They recommend the sequence

$$45_0 180_{90} 90_{180} 180_{90} 45_0 \tag{117}$$

as a composite 180° pulse in solids. It is perhaps easiest to see that this also has $\bar{H}^{(0)} = 0$ by noting that it may be derived from (116) by permuting a 45_0 pulse; It may be shown that if a sequence has a vanishing average Hamiltonian, this will remain true if an element is permuted which commutes with the overall propagator, which is the case here. Tycko *et al.*(45) performed computer simulations and experiments on systems with small numbers of dipolar-coupled spins and could verify the improved population inversion. However the hopes for universality of such sequences were only

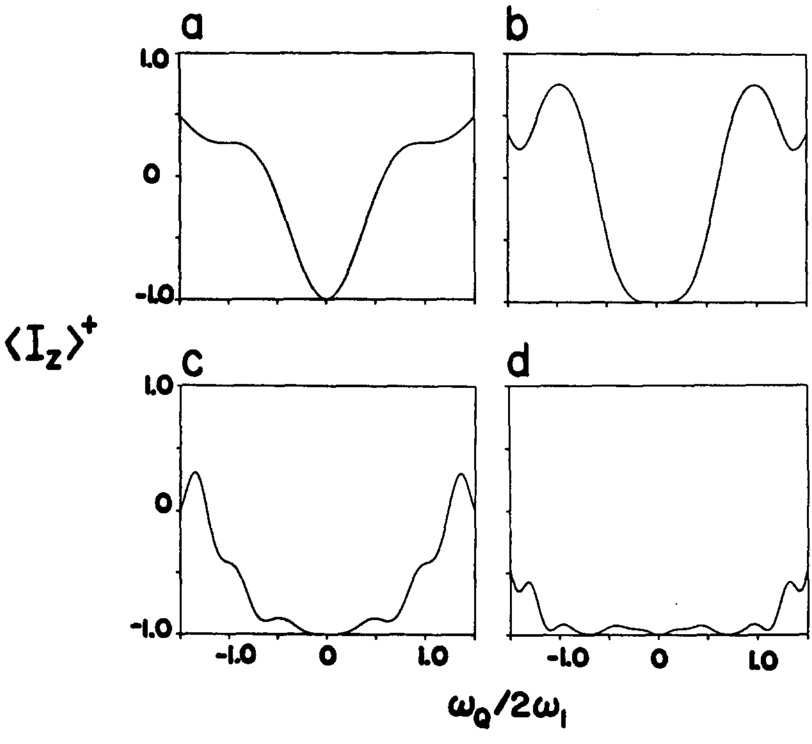

FIG. 21. Numerical simulations of $\langle I_z \rangle^+$ for spin $I=1$ as a function of quadrupolar splitting $\omega_Q/2\omega_1$ for the sequences (a) 180_0, (b) $90_0 180_{90} 90_{180} 180_{90}$,[115] (c) $45_0 180_{90} 90_{180} 180_{90} 45_0$,[45] (d) $45_0 90_{180} 135_0 45_{90} 90_{270} 135_{90} 45_0 90_{180} 135_0$.

partially satisfied. The enhancement of the spin inversion as against a single pulse, as predicted by numerical simulation, was strongly dependent on the configuration of the couplings between the spins. Also experimental results for squaric acid, which contains large numbers of coupled spins, were only presented for very low r.f. fields of 20 kHz, although r.f. fields exceeding 80 kHz are easily available. The variability in the performance of such sequences arises because of slow convergence of the Magnus expansion in realistic cases. In principle, some of the higher terms may be eliminated by using longer pulse sequences, but no such sequence has yet been suggested for arbitrary second-rank interactions. (The technique of 'symmetrization', mentioned above, may be used for *cyclic* sequences to eliminate all odd terms $\bar{H}^{(m)(1\,0)}$, but no such possibility is yet known for non-cyclic composite pulses.)

Nevertheless, $45_0 180_{90} 90_{180} 180_{90} 45_0$ is a useful composite 180° pulse for isolated spins $I=1$ or small numbers of coupled spins-1/2. In Fig.21, computer simulations of $\langle I_z \rangle^+$ for a single spin-1 system are shown for this sequence as well as for a single 180° pulse and the BLEW-6 sequence $90_0 180_{90} 90_{180} 180_{270}$. These simulations were produced using a numerical diagonalization of the Hamiltonian in the presence of the r.f. field. The bandwidth of the inversion for the composite pulses is clearly greater than for a single 180° pulse. Also shown in this diagram is the performance of the sequence $45_0 90_{180} 135_0 45_{90} 90_{270} 135_{90} 45_0 90_{180} 135_0$ to be described below. Experimental results obtained with the deuterium (spin 1) solid-state spectra of polycrystalline d^5-phenylalanine are shown in Fig.22. These were obtained by measuring the z-magnetization immediately after a

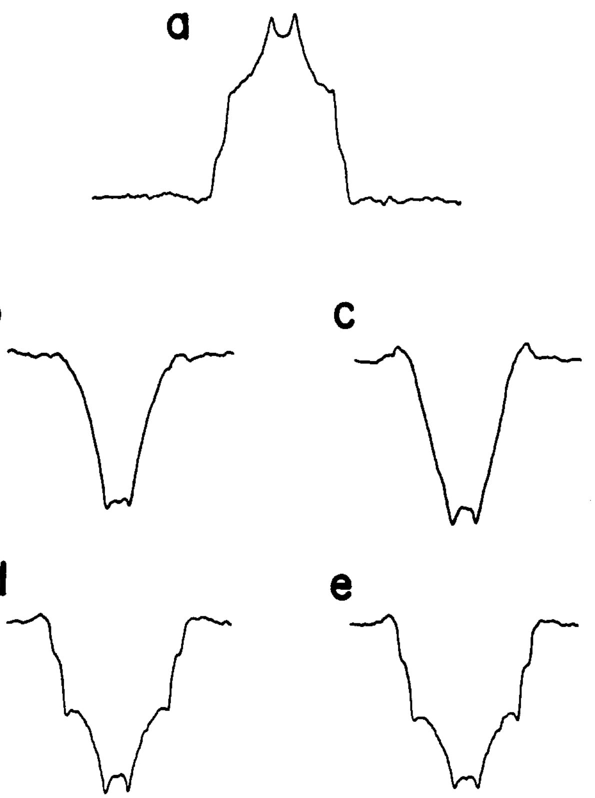

FIG. 22. Experimental ^{2}D lineshapes of d^5-phenylalanine, obtained at 46 MHz by composite pulse echoes preceded by a composite 180° pulse, with 4-step phase cycling to select the longitudinal component after the 180° pulse. The full width of the line is 130 kHz, the r.f. field was $\omega_1/2\pi = 59.5$ kHz. (a) No inversion pulse, (b) after 180_0, (c) after $90_0 180_{90} 90_{180} 180_{90}$ (d) after $45_0 180_{90} 90_{180} 180_{90} 45_0$, (e) after $45_0 90_{180} 135_0 45_{90} 90_{270} 135_{90}$ $45_0 90_{180} 135_0$. The 'horns' in (d) and (e) are possibly the result of molecular motion on the timescale of the inversion pulse.

(composite) 180° pulse by using the quadrupolar echo sequence $45_0 90_{180} 135_0 - \tau_1 - 45_{90} 90_{270} 135_{90} - \tau_2$ (next Section). The 180° pulse was cycled through four orthogonal phases with signals added so as to suppress single or double quantum coherence unintentionally created by the inversion pulse. The single 180° pulse clearly achieves good inversion only for those crystallites in such orientations that the quadrupolar tensor is small. This seriously interferes with spin–lattice relaxation time measurements, especially when the spectral variation of T_1 is of interest.[116] The increased bandwidth of the composite pulses is obvious from the improved appearance of the inverted spectral line shapes. The spectra shown were obtained with a moderate r.f. field strength of $\omega_1/2\pi = 54.3$ kHz (corresponding to a 90° pulse of duration 4.6μsec).

Tycko has also suggested the sequence $45_0 135_{180} 135_{90} 45_{270}$ as a composite 90° pulse in systems with second-rank interactions.[44] However this sequence seems to suffer particularly badly from the slow convergence of the Magnus expansion and its performance is disappointing.

8.2. *Consecutive Rotation Method*

Systems of isolated pairs of equivalent dipolar coupled spins-1/2, or isolated spin $I=1$ systems, are simple enough that the dynamics during a pulse or arbitrary frequency or field strength may be solved analytically.[116–121] In the following we refer only to the spin $I=1$ problem, but all conclusions also apply to spin-1/2 pairs if the words 'quadrupolar interaction' are replaced by 'dipolar interaction'. In these systems there are three relevant eigenstates which are in general unequally spaced. The difference between the spacing between states $|1\rangle$ and $|2\rangle$ from that between states $|2\rangle$ and $|3\rangle$ is given by the quadrupolar interaction $2\omega_Q$. This 'anharmonicity' varies according to the orientation of the tensor with respect to the static magnetic field, giving rise to the well-known 'powder lineshapes' for non-oriented samples.

Imperfect pulse performance arises because the r.f. field cannot be on resonance for both single-quantum transitions simultaneously, unless the quadrupolar splitting is very small. However it is usually possible to apply the irradiation very close to the mean frequency of the two transitions, which is only affected by relatively small second-order quadrupolar and chemical shift interactions. The system is then discribed by a single unknown, the quadrupolar splitting.

The Hamiltonian in the presence of an r.f. field of phase ϕ is given by

$$H_\phi = H_Q + \omega_1 \exp(-i\phi I_z) I_x \exp(i\phi I_z) \tag{118}$$

where the first-order quadrupolar interaction is given by

$$H_Q = \omega_Q \tfrac{1}{3}(3I_z{}^2 - I(I+1)) \tag{119}$$

The non-commutation of the two terms in eqn.(118) is the cause of the trouble.

It is convenient to express all interactions in terms of the single-transition operators,[120,121] defined by

$$\begin{aligned} I_z^{(rs)} &= \tfrac{1}{2}(|r\rangle\langle r| - |s\rangle\langle s|) \\ I_x^{(rs)} &= \tfrac{1}{2}(|r\rangle\langle s| + |s\rangle\langle r|) \\ I_y^{(rs)} &= \tfrac{1}{2i}(|r\rangle\langle s| - |s\rangle\langle r|) \end{aligned} \tag{120}$$

which have cyclic commutation relationships, for example

$$[I_x^{(rs)}, I_y^{(rs)}] = i\, I_z^{(rs)} \tag{121}$$

and

$$[I_x^{(rs)}, I_x^{(st)}] = \tfrac{1}{2} i\, I_y^{(rt)}. \tag{122}$$

It is also convenient to introduce quadrupole polarization operators[39] $Q_z^{(rs)}$ defined by

$$Q_z^{(rs)} = \tfrac{2}{3}(I_z^{(rt)} + I_z^{(st)}) \tag{123}$$

with properties

$$
\begin{aligned}
&[Q_z^{(rs)}, I_v^{(rs)}] = 0, \qquad v = x,y,z;\\
&Q_z^{(rs)} = Q_z^{(sr)}; \qquad Q_z^{(rs)} + Q_z^{(st)} + Q_z^{(tr)} = 0;\\
&Q_z^{(rs)} = I_z^{(rt)} - \tfrac{1}{2}Q_z^{(rt)}; \qquad I_z^{(rs)} = \tfrac{1}{2}(Q_z^{(rt)} - Q_z^{(st)}).
\end{aligned} \tag{124}
$$

Then we may write

$$
\begin{aligned}
I_x &= 2^{1/2}(I_x^{(1\,2)} + I_x^{(23)})\\
I_y &= 2^{1/2}(I_y^{(1\,2)} + I_y^{(23)})\\
I_z &= 2I_z^{(1\,3)}
\end{aligned}
$$

and

$$H_Q = \omega_Q Q_z^{(1\,3)}$$

The Hamiltonian may be put in a more tractable form by expressing all operators in the '$U_y^{(1\,3)}$ frame' defined by the transformation

$$A^T = \exp(i\frac{\pi}{2}I_y^{(1\,3)})\ A\ \exp(-i\frac{\pi}{2}I_y^{(1\,3)}). \tag{125}$$

By using eqns (121) and (122), the operators I_x, I_y and I_z become in this frame $I_x{}^T = 2I_x{}^{(1\,2)}$, $I_y^T = 2I_y{}^{(23)}$ and $I_z^T = -2I_x{}^{(1\,3)}$. The quadrupole term $Q_z^{(1\,3)}$ is unchanged. The Hamiltonians during pulses of phase $\phi = 0, 90°, 180°$ and $270°$ are:

$$
\begin{aligned}
H^T_{\phi=0} &= (\omega_Q I_z^{(1\,2)} + 2\omega_1 I_x^{(1\,2)}) - \tfrac{1}{2}\omega_Q Q_z^{(1\,2)}\\
H^T_{\phi=90} &= (-\omega_Q I_z^{(23)} + 2\omega_1 I_y^{(23)}) - \tfrac{1}{2}\omega_Q Q_z^{(23)}\\
H^T_{\phi=180} &= (\omega_Q I_z^{(1\,2)} - 2\omega_1 I_x^{(1\,2)}) - \tfrac{1}{2}\omega_Q Q_z^{(1\,2)}\\
H^T_{\phi=270} &= (-\omega_Q I_z^{(23)} - 2\omega_1 I_y^{(23)}) - \tfrac{1}{2}\omega_Q Q_z^{(23)}.
\end{aligned} \tag{126}
$$

Suppose we wish to design a composite 90° pulse. In the $U_y^{(1\,3)}$ frame, this implies we wish to be able to take the spin system from an initial condition $I_z^T = -2I_x^{(1\,3)}$ to a final state $-I_y{}^T = -2I_y^{(23)}$. Neglecting the unimportant change of subscript, this implies an interchange of states $|1\rangle$ and $|2\rangle$ in this frame. Now from eqn.(126), a pulse of phase $\phi = 0$ or $\phi = 180°$ acts as an effective rotation on the $|1\rangle \leftrightarrow |2\rangle$ transition in the $U_y^{(1\,3)}$ frame; to interchange states $|1\rangle$ and $|2\rangle$, we require a 180° pulse in this space; this leads to the surprising corollary that a composite 90° pulse in a three-level system has more in common with a 180° spin-1/2 pulse than with a 90° spin-1/2 pulse. If these suspicions are taken to their logical conclusion it may be shown[39] that a 180° pulse for spins-1/2 may be converted to a 90° pulse for spins-1 simply by dividing all pulse lengths by two, if the following conditions are met:

(a) only 180° phase shifts are involved;

(b) if the 180° pulse is of type B, then the phase of the overall rotation operator must be linearly dependent on offset.

The pulse lengths should be divided by two because of the factor 2 in the term proportional to ω_1 in eqn.(126). Condition (a) is also a consequence of eqns(126), which show that pulses of phases other than 0 and 180° do not provide the necessary pure rotations in the $|1\rangle \leftrightarrow |2\rangle$ space. Condition (b) arises because a linear offset-dependent phase shift of the spin-1/2 180° composite pulse is converted into an apparent *time shift* of the free induction decay after the spin-1 90° composite pulse. For powder spectra, it is essential to ensure that the time shift is uniform so that all signal components echo simultaneously (see below).

Both conditions are met to a fair approximation by the two spin-1/2 180° composite pulses encountered earlier, $90_0 180_{180} 270_0$ and $90_0 270_{180} 180_0 360_{180} 180_0$. These are both broadband 180°

pulses and the last also gives a nicely linear dependence of the phase on offset, with a propagator given to a good approximation by

$$\exp(-i\frac{\Omega^0}{\omega_1}I_z)\exp(-i\pi I_x)\exp(i\frac{\Omega^0}{\omega_1}I_z). \tag{127}$$

For the shorter sequence however, the phase-dependence shows appreciable deviations from linearity. This is of consequence when fine details of the quadrupolar lineshapes are of interest (see below).

With pulse lengths divided by two, these sequences have propagators given in the $U_y^{(13)}$ frame approximately by

$$U^T \simeq \exp(-i\theta_a Q_z^{(13)})\exp(-i\theta_b Q_z^{(23)})\exp(-i\pi I_x^{(12)}) \tag{128}$$

where

$$\theta_a = \tfrac{1}{2}(\omega_Q T + \omega_Q/\omega_1)$$

and

$$\theta_b = \tfrac{1}{2}(\omega_Q T - \omega_Q/\omega_1) \tag{129}$$

Here T is the total duration of the composite pulse. In eqn.(128), the rightmost operator induces the necessary interchange of states $|1\rangle$ and $|2\rangle$, the operator $\exp(-i\theta_b Q_z^{(23)})$ commutes with the final condition I_y^T, whilst the leftmost operator $\exp(-i\theta_a Q_z^{(13)})$ is responsible for the time-shift alluded to above. Thus sequences such as $45_0 90_{180} 135_0$ and $45_0 135_{180} 90_0 180_{180} 90_0$ give broadband excitation of coherence in spin-1 systems.[39]

They may also be incorporated into quadrupole echo sequences[122] which are widely used in solid-state deuterium NMR to make accessible the first few points of the free-induction transient. Two composite pulses are applied with a phase difference of 90° separated by a time τ_1; the echo occurs at time τ_2 given by, assuming eqn.(129) is valid,

$$\tau_2 = \tau_1 + T/2 + 1/(2\omega_1) \tag{130}$$

Composite pulse echoes are a particularly important technique because the use of two 90° pulses seriously aggravates the effect of insufficient r.f. field when single 90° pulses are used; the previous solutions to this problem were to use pulses much shorter than 90°, or to multiply the spectrum by a frequency-dependent correction factor which may be calculated analytically. The first of these methods leads to a large loss in signal intensity, and the second is only feasible when the distortions are relatively small. Composite pulses allow work with much lower r.f. fields than currently used, with large advantages in instrumental stability and much smaller heating effects.

The performance of composite pulse echo sequences has been studied by computer simulation and by experiment; the conclusions outlined above have been generally vindicated. Figure 23 shows simulated intensities of y-magnetization at times given by eqn.(130) for the two composite pulse sequences, and at the theoretical echo maximum given by $\tau_2 = \tau_1 + T/2$[118] for a conventional two-pulse echo 90_0–τ_1–90_{90}–τ_2. The dependence of magnetization on the size of the quadrupole is clearly much reduced. In Fig.24 are shown some typical experimental results for d^5-phenylalanine, with a fairly low r.f. field corresponding to a 90° pulse length of 6.2μsec. Here the echo sequence $45_0 90_{180} 135_0$–τ_1–$45_{90} 90_{270} 135_{90}$ was used.

Broadband population inversions of spins-1 can also be created by this type of pulse sequence by placing together three composite pulses, of phases 0,90 and 0. For example the sequence $45_0 90_{180} 135_0 45_{90} 90_{270} 135_{90} 45_0 90_{180} 135_0$ performs quite well in comparison with the sequences derived by coherent averaging theory, as has been demonstrated above. The propagator for such sequences may be written

$$\begin{aligned} U^T \simeq\ & \exp(-i\theta_a Q_z^{(13)})\exp(-i\theta_b Q_z^{(23)})\exp(-i\pi I_x^{(12)}) \\ & \times \exp(-i\theta_a Q_z^{(13)})\exp(-i\theta_b Q_z^{(12)})\exp(-i\pi I_y^{(23)}) \\ & \times \exp(-i\theta_a Q_z^{(13)})\exp(-i\theta_b Q_z^{(23)})\exp(-i\pi I_x^{(12)}) \end{aligned} \tag{131}$$

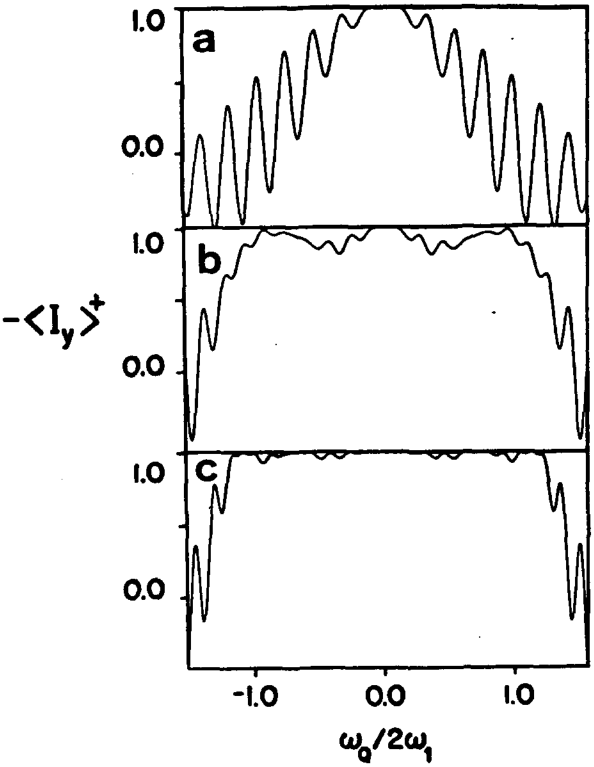

FIG. 23. Simulations of the y-magnetization $\langle I_y \rangle^+$ for spin 1 as a function of the quadrupolar splitting for the quadrupolar echo sequences (a) $90_0-\tau_1-90_{90}-\tau_2$; $\tau_2=\tau_1+\pi/(4\omega_1)$. (b) $45_0 90_{180} 135_0-\tau_1-45_{90} 90_{270} 135_0-\tau_2$; $\tau_2=\tau_1+(3\pi+2)/(4\omega_1)$. (c) $90_0 180_{180} 90_0 135_{180} 45_0-\tau_1-90_{90} 180_{270} 90_{90} 135_{270} 45_{90}-\tau_2$; $\tau_2=\tau_1+(6\pi+2)/(4\omega_1)$. (From Ref. 39.)

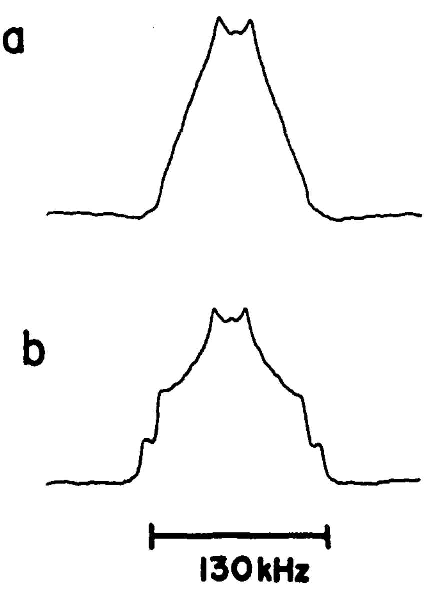

FIG. 24. Experimental spectral lineshapes for d^5-phenylalanine after the quadrupolar echo sequences (a) $90_0-\tau_1-90_{90}-\tau_2$, (b) $45_0 90_{180} 135_0-\tau_1-45_{90} 90_{270} 135_{90}-\tau_2$. The r.f. field strength was $\omega_1/2\pi=40.3$ kHz.

which may be rearranged as

$$U^T \simeq \exp\{-i(\theta_a+\theta_b)(Q_z^{(13)}+Q_z^{(23)}+Q_z^{(12)})\} \times \exp(-i\pi I_x^{(12)})\exp(-i\pi I_y^{(23)})\exp(-i\pi I_x^{(12)}) \tag{132}$$

by using such properties as

$$\exp(-i\pi I_x^{(rs)})Q_z^{(rt)} = Q_z^{(rt)}\exp(-i\pi I_x^{(rs)}) \tag{133}$$

Now the first term in eqn. (132) is unity through eqn. (124), and the last three terms, on transformation into the laboratory frame become

$$\begin{aligned} U &\simeq \exp(-i\tfrac{\pi}{2}I_x)\exp(-i\tfrac{\pi}{2}I_y)\exp(-i\tfrac{\pi}{2}I_x) \\ &= \exp(-i\tfrac{\pi}{4}I_z)\exp(-i\pi I_x)\exp(i\tfrac{\pi}{4}I_z). \end{aligned} \tag{134}$$

This is a 180° rotation with a phase of 45°. It is likely that more compact inversion pulses for spins $I=1$ can also be produced using the same formulation, but none have so far been discovered.

There are a number of subtleties when applying all of these pulse sequences to systems of practical interest. Firstly, transient effects arising when suddenly turning on the pulse or switching its phase in the tuned resonance circuit were neglected, as was the finite bandwidth of the probe when observing the NMR signal. Both of these effects are significant for very wide quadrupolar spectra. Secondly, the above treatment assumed a quadrupolar tensor which is static on the time-scale of the pulse sequence, which is valid in the very fast or very slow motion regimes. But if motion on an intermediate time scale is present, the effect of the composite pulse is not as simple as presented here and must be analyzed by more sophisticated methods. Strange lineshape distortions due to motional effects have indeed been observed when using composite pulses.[123] Thirdly, Olejniczak *et al.*[123] have pointed out that quadrupolar echoes using the pulse sequence $45_0 90_{180} 135_0$ can produce slightly distorted lineshapes even in the absence of motion, which is because the phase shift term in eqn.(127) is not closely linear for this sequence, so that different echo components may refocus at slightly different times. The distortions are however almost absent if $45_0 135_{180} 90_0 180_{180} 90_0$ is used.

8.3. *Double-Quantum Excitation*

Another manipulation often performed on spins $I=1$ in solids, other than inversion of population and excitation of single-quantum coherence, is excitation of coherence between the two extreme eigenstates $|1\rangle$ and $|3\rangle$. In high field, double-quantum coherence does not provide a macroscopic magnetic dipole moment and cannot be observed directly, but its precession may be made visible by transfer to single-quantum coherence by a suitable pulse sequence and employing a variant of two-dimensional spectroscopy.[2] Double-quantum coherence of spins $I=1$ is insensitive to the first-order quadrupolar interaction and hence can allow measurement of chemical shift tensors which are normally buried under this much larger term.[124] In combination with magic-angle spinning, deuterium double-quantum coherence can provide liquid-like isotropic shift spectra from solid samples in favourable cases.[125]

Double-quantum coherence is most often excited by a simple pair of strong 90° pulses. (A centrally placed 180° pulse can also be included to remove dependence on chemical shifts.) The efficiency of excitation is given by $\sin(\omega_Q\tau)$, where τ is the separation of the pulses, and if a third pulse is applied and the echo taken at a further time τ, the intensity of the signal is proportional to $\sin^2(\omega_Q\tau)$, assuming uniform spin–spin relaxation times. If the first two pulses are separated by a time longer than the inverse of the powder linewidth, so that the inhomogeneously damped free induction response produced by the first pulse has vanished when the second is applied, the fast oscillating contributions may be ignored, giving an uniform intensity of 1/2 for the double-quantum transferred signal, independent of ω_Q. This condition may be referred to as 'uniform double-quantum excitation', and is desirable because only under these conditions can the chemical shift tensor be easily extracted from the double-quantum spectrum.

There are a number of problems with this method, however. Firstly, waiting a long time before the second pulse is applied results in an appreciable loss of signal. Any sharp singularities in the spectrum extend the free induction decay considerably but must be allowed to decay. Secondly, in cases with motion the transverse relaxation times vary across the spectrum and again cause non-uniform double-quantum intensities. Thirdly, if the pulse power is limited, the outer edges of the spectrum are poorly excited (this can of course be overcome by using composite pulses of the type discussed above). These problems have stimulated attempts to find different ways of exciting double-quantum coherence uniformly.

A suggestion has been made by Barbara *et al.*[111] They noted that if the pulses are strong with respect to the quadrupole interaction, the sequence 90_{90}–$\tau/2$–180_{270}–$\tau/2$–90_{90} has a propagator

$$U = \exp(-i\omega_Q \tau I_x^{(13)}) \exp(-i\frac{\omega_Q}{2}\tau Q_z^{(13)}). \tag{135}$$

The term on the left is a rotation in the double-quantum space through an angle $\omega_Q\tau$ and the term on the right commutes with it. The sequence can therefore be compensated for the effects of variation in ω_Q by methods analogous to compensation of r.f. field variations in spin-1/2 pulses. A difference is that phase shifts of ϕ in ordinary space are experienced as 2ϕ in double-quantum space, so all pulse *phases* must be divided by two if the compensation effect is to be retained (this is reminiscent of, but not the same as, the division of all pulse *lengths* by two in the previous section). For example the A-type composite 90° pulse $270_0 360_{169} 180_{33} 180_{178}$ suggested by Tycko[48] can be converted, with a bit of jiggery-pokery, into the quadrupole-compensated double-quantum excitation sequence[111]

$$90_0\text{–}3\tau/2\text{–}180_{180}\text{–}3\tau/2\text{–}95.5_{90}\text{–}2\tau\text{–}180_0\text{–}2\tau\text{–}112_{90}\text{–}\tau\text{–}180_{180}\text{–}\tau\text{–}107.5_{90}\text{–}\tau\text{–}180_0\text{–}\tau\text{–}90_{180}. \tag{136}$$

The sequence was tried out in the oriented spin-1/2 pair of CH_2Cl_2 dissolved in a liquid crystal and some increased insensitivity to the magnitude of the coupling could be demonstrated (in fact, the effect of the magnitude of the dipolar coupling was simulated by changing the value of the delays between pulses). However, there are good reasons to believe such sequences will not behave very well in cases of practical importance: (a) their duration is very long, so a loss of signal possibly even greater than with the two pulse sequence is to be expected through transverse relaxation; (b) compensation is to be expected only if the transverse relaxation times are uniform; and (c) the 'bandwidth' achieved is slightly greater than with just two pulses, but appears insufficient to make measurement of undistorted chemical shift tensors feasible. Nevertheless, the principle is interesting, and some of the other directions suggested, such as compensated double-quantum excitation by long single pulses applied near the mean frequency of the single-quantum transitions,[117] or by modulated pulses,[78] or compensated double-quantum excitation in two-spin systems in isotropic liquids, might be more practical.

8.4. *Quadrupolar Order*

We should also mention the excitation of quadrupolar order $Q_z^{(13)}$ in spin $I = 1$ systems, which is important in measurement of slow molecular motions.[126] The usual excitation sequence is 90_0–τ–45_{90}, with a subsequent 45_0 pulse for observation of the quadrupolar order (Jeener–Broekaert sequence.[63]) The 45° pulses are rather insensitive to the quadrupolar interaction and need not be compensated[119] (They behave analoguously to 90° pulses in spin-1/2 systems.) The excitation may however be improved by replacing the first 90_0 pulse by a composite sequence such as $45_0 135_{180} 90_0 180_{180} 90_0$.

9. CONCLUDING REMARKS

The subject of composite pulses has many facets. They may be viewed as a purely technical device to achieve improved pulse performance; their value may be assessed more as a stimulation to think more deeply about the operation of particular NMR experiments (decoupling is a good example); they have also provoked interest as an abstract exercise in non-linear dynamics, in a system which is experimentally well-defined, simple enough for exhaustive numerical calculation, and yet complex enough to provide surprises and challenging unsolved problems. The number of different ways of producing composite pulses which have been advocated, and the conflicting interpretations which have appeared in the literature, often bordering on controversy, are evidence enough of that. And yet composite pulses are very easy to treat compared with continuous modulation techniques, the theory of which is still in its infancy.

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