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A General Theory of Multiple Spin Echoes

A theory has been developed for the amplitudes and shapes of a series of spin echoes produced by a train of rectangular pulses of arbitrary number, amplitude, duration and time sequence. The treatment is based upon Jaynes' method[1] of solving the Bloch equation in terms of the 2×2 rotation matrices of spinor theory. Whereas the formalism set up by Jaynes' for the solution of special cases requires matrix elements to be multiplied out at length, the present method manipulates the non-commutative algebra of the matrix formulas to arrive at the required results directly. To illustrate the method, we consider the case (see Fig. 1) in which a train of uniform pulses applied in arbitrary time sequence is made to produce a series of "stimulated normal order echoes."[2] We must determine the motion of the magnetization $\mathbf{M}(\Delta\omega)$ by solving the Bloch equation without relaxation terms. If the pulse train be generated by an amplitude modulated oscillator, the Bloch equation may be written in a rotating frame of reference as[3]

$$\frac{\partial \mathbf{M}}{\partial t}(\Delta\omega)+\gamma[\mathbf{H}_{er}\times\mathbf{M}(\Delta\omega)]=0, \qquad (1)$$

[1] E. T. Jaynes', Phys. Rev. **98**, 1099 (1955).
[2] A. G. Anderson, R. L. Garwin, E. L. Hahn, J. W. Horton, G. L. Tucker, R. M. Walker, J. of Applied Physics, **26**, 1324 (1955).
[3] I. Rabi, N. Ramsey, S. Schwinger, Rev. Modern Phys., **26**, 167 (1954).

where $\mathbf{H}_{er}$, "the effective field," is constant during each pulse and is

$$\mathbf{H}_{er}=\mathbf{H}_1+\mathbf{\Delta\omega}/\gamma.$$

In this frame $\mathbf{M}(\Delta\omega)$ satisfies (1) if it rotates about $\mathbf{H}_{er}$ with angular velocity $b=[(\gamma H_1)^2+(\Delta\omega)^2]^{\frac{1}{2}}$. In Fig. 1 we show H_1 as a function of time. For simplicity let us assume that $\mathbf{M}(\Delta\omega)$ rotates only about $\mathbf{H}_1$ during each pulse, i.e. that $\Delta\omega/\gamma\ll H_1$. Following Jaynes, each rotation of $\mathbf{M}(\Delta\omega)$ is represented by a 2×2 rotation matrix $\mathbf{Q}_i$, and the resultant rotation of a series of rotations may be represented by a matrix $\mathbf{Q}$ which is given by the product of the individual rotation matrices $\mathbf{Q}_i$. If the initial magnetization is in the z-direction and normalized to unit magnitude, i.e. if $\mathbf{M}_0(\Delta\omega)=1\mathbf{k}$, and if $\mathbf{Q}$ rotates $\mathbf{M}_0$ into $\mathbf{M}$ where

$$\mathbf{Q}=\begin{pmatrix}\alpha & \beta\\ -\beta^* & \alpha^*\end{pmatrix}, \qquad (2)$$

then the y-component of $\mathbf{M}(\Delta\omega)$ can be shown to be

$$M_y(\Delta\omega)=i(\alpha^*\beta^*-\alpha\beta). \qquad (3)$$

If $g(\Delta\omega)$, the distribution or weighting function of $\mathbf{M}(\Delta\omega)$ over the sample,[4] be a symmetric function in $\Delta\omega$, i.e. if

[4] E. L. Hahn, Phys. Rev., **80**, 580 (1950).

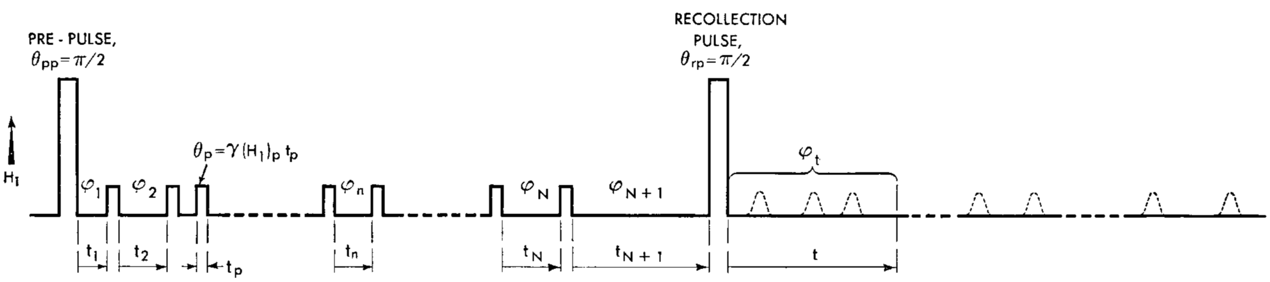

Figure 1

Pulse amplitude H_1 in the rotating frame versus time, t, for production of a train of normal order spin echoes. In the case illustrated, N identical "information" pulses are applied at arbitrary times. During each pulse $\mathbf{M}(\Delta\omega)$ is assumed to rotate only about $\mathbf{H}_1$ through the angles shown; between pulses $\mathbf{M}(\Delta\omega)$ precesses freely about the z-axis through angles $\varphi_j=\Delta\omega t_j$. The times of occurrence of desired normal order echoes are indicated; the undesired or "interpulse" echoes[2] are not shown.

$g(\Delta\omega)=g(-\Delta\omega)$, then only $M_y(\Delta\omega)$ is needed to find the shapes and amplitudes of the spin echoes. It is useful to define two matrices **A** and **B** such that

$$\mathbf{A}=\begin{pmatrix}\alpha & 0\\ 0 & \alpha^*\end{pmatrix},\qquad \mathbf{B}=\begin{pmatrix}0 & \beta\\ -\beta^* & 0\end{pmatrix},\tag{4}$$

for then $\mathbf{Q}=\mathbf{A}+\mathbf{B}$, and $M_y(\Delta\omega)$ has the matrix form

$$M_y(\Delta\omega)=(-i)Tr(\mathbf{A}^*\boldsymbol{\sigma}_x\mathbf{B}),\tag{5}$$

where Tr denotes the trace of matrix $(\mathbf{A}^*\boldsymbol{\sigma}_x\mathbf{B})$.

Jaynes gives an exponential and a binomial form which express the individual rotation matrices $\mathbf{Q}_i$ explicitly in terms of the rotation angle θ and the unit vector **n** in the direction of the rotation axis. These forms are

$$\mathbf{Q}_i=\exp(-\tfrac{1}{2}i\mathbf{n}\cdot\boldsymbol{\sigma}\theta)=\mathbf{1}\cos(\tfrac{1}{2}\theta)-i\mathbf{n}\cdot\boldsymbol{\sigma}\sin(\tfrac{1}{2}\theta).\tag{6}$$

The vector $\boldsymbol{\sigma}$ has components $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, $\boldsymbol{\sigma}_z$ which are the Pauli spin matrices.[1] Using (6) to describe the rotations indicated in Fig. 1, we may write **Q** at time t after the second 90° pulse as

$$\mathbf{Q}=\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z\phi_t)\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_x\pi/2)\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z\phi_{N+1})$$

$$(\mathbf{c}-is\boldsymbol{\sigma}_x)\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z\phi_N)\cdots\cdots\exp(-\tfrac{1}{2}\boldsymbol{\sigma}_z\phi_2)(\mathbf{c}-is\boldsymbol{\sigma}_x)$$

$$\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z\phi_1)\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_x\pi/2)\tag{7}$$

where

$$\mathbf{c}\equiv\mathbf{1}\cos(\tfrac{1}{2}\theta_p),\ s\equiv\sin(\tfrac{1}{2}\theta_p)\tag{8}$$

and

$$\theta_p=(H_1)_p t_p,\ \varphi_j=\Delta\omega t_j,\ \varphi_t=\Delta\omega t.\tag{9}$$

In (7) the exponential and binomial forms of (6) have been used respectively for periods of free precession and for pulse rotations. From the anti-commutation property of the Pauli spin matrices, specifically that $\boldsymbol{\sigma}_x\boldsymbol{\sigma}_z=\boldsymbol{\sigma}_z\boldsymbol{\sigma}_x$, there follows the commutation relation

$$\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z)\boldsymbol{\sigma}_x=\boldsymbol{\sigma}_x\exp(\tfrac{1}{2}i\boldsymbol{\sigma}_z).\tag{10}$$

Using (10) to move the exponentials in (7) to the right, and using (6) with $\theta=\pi/2$, **Q** can be written

$$\mathbf{Q}=\tfrac{1}{2}\mathbf{Z}\,(\mathbf{1}-\boldsymbol{\sigma}_x)\mathbf{P}\mathbf{Z}(\mathbf{1}-\boldsymbol{\sigma}_x),\tag{11}$$

where

$$\mathbf{P}\equiv\left(\mathbf{c}-is\boldsymbol{\sigma}_x\ \exp[i\boldsymbol{\sigma}_z\phi_{N+1}]\right)\ \left(\mathbf{c}-is\boldsymbol{\sigma}_x\ \exp[i\boldsymbol{\sigma}_z(\phi_{N+1}+\phi_N)]\right)$$

$$\cdots\left(\mathbf{c}-is\boldsymbol{\sigma}_x\ \exp[i\boldsymbol{\sigma}_z(\phi_{N+1}+\cdots+\phi_2)]\right)\tag{12}$$

and

$$\mathbf{Z}_t\equiv\exp(-\tfrac{1}{2}i\boldsymbol{\sigma}_z\phi_t),$$

$$\mathbf{Z}\equiv\exp[-\tfrac{1}{2}\boldsymbol{\sigma}_z(\phi_{N+1}+\phi_N+\cdots+\phi_1)].\tag{13}$$

If **P** be multiplied out, the commutation relation (10), together with the property of a Pauli spin matrix that $\boldsymbol{\sigma}_x{}^2=\mathbf{1}$, may be used to express **P** in the binomial form

$$\mathbf{P}=\mathbf{P}_1-i\boldsymbol{\sigma}_x\mathbf{P}_2.\tag{14}$$

The functions $\mathbf{P}_1$ and $\mathbf{P}_2$ are polynomials in the variables **c** and s with coefficients which are the sum of products of matrices of the form $\exp(i\boldsymbol{\sigma}_z\phi)$. The significance of (14), since $\boldsymbol{\sigma}_x$ does not appear in $\mathbf{P}_1$ or $\mathbf{P}_2$ is that the terms of $\mathbf{P}_1$ and $\mathbf{P}_2$ may be handled by the rules of ordinary, commutative algebra. Furthermore, $\mathbf{P}_1$ and $\mathbf{P}_2$ commute with each other and with all other matrices of form $\exp(i\boldsymbol{\sigma}_z\phi)$, such as $\mathbf{Z}_t$ and **Z**. If (14) is substituted in (11), **Q** may be expressed as the sum of eight terms each of form $\mathbf{Z}_t\cdot\mathbf{P}_1\mathbf{Z}$. From this expression, $\mathbf{A}^*$ and $\boldsymbol{\sigma}_x\mathbf{B}$ are readily obtained as the sum of four terms each. The matrix $\mathbf{A}^*\cdot\boldsymbol{\sigma}_x\mathbf{B}$ thus consists of 16 terms, but of these only two have the time dependence characteristic of the direct order echoes desired in practice. Consequently, for desired, direct order echoes, it is found that

$$M_y(\Delta\omega)=\tfrac{1}{2}Tr[(\mathbf{Z}_{-t}\mathbf{Z})^2\cdot\mathbf{P}_1\mathbf{P}_2],\tag{15}$$

where $\mathbf{Z}_{-t}\equiv\exp(\tfrac{1}{2}i\boldsymbol{\sigma}_z\Delta\omega t)$. Form (15) is a central result of this method. Special algebraic methods are developed to pick from $\mathbf{P}_1\mathbf{P}_2$ those terms which contribute to the echo of the nth pulse. The sum of these terms, once identified, is readily obtained, and the result is that $M_y(\Delta\omega)$ for the echo of the nth pulse is

$$M_y(\Delta\omega)]_n=\tfrac{1}{2}Tr[\mathbf{D}_n\exp(i\boldsymbol{\sigma}_z\Delta\omega\tau)],\tag{16}$$

where $\tau=t-(t_1+t_2+\cdots\cdots t_n)$, and the echo amplitude function $\mathbf{D}_n$ obtained from $\mathbf{P}_1\mathbf{P}_2$ is

$$\mathbf{D}_n=\mathbf{1}\cdot D_n=\mathbf{1}\cdot sc\cdot(c^2)^{n-1}(c^2-s^2)^{N-n},\tag{17}$$

where s and θ_p are given in (8) and (9), and $c\equiv\cos(\theta_p/2)$. $\mathbf{D}_n$ is independent of $\Delta\omega$. The echo of the nth pulse is found by integrating (16) over $g(\Delta\omega)$.[4] It is

$$[\overline{M}_y(t)]_n=\tfrac{1}{2}\int Tr[\mathbf{D}_n\exp(i\boldsymbol{\sigma}_z\Delta\omega\tau)]\cdot g(\Delta\omega)d(\Delta\omega).\tag{18}$$

$\overline{M}_y(t)$ is the y-component in the rotating frame of the magnet moment $\overline{\mathbf{M}}(t)$ of the sample at time t, which is

$$\overline{\mathbf{M}}(t)=\int\mathbf{M}(\Delta\omega,t)g(\Delta\omega)d(\Delta\omega),$$

$$\text{where}\quad\int g(\Delta\omega)d(\Delta\omega)=1.\tag{19}$$

The peak of the echo occurs at time $t'=t_1+\cdots+t_n$, or when $\tau=0$; hence as follows from (19) and the fact that $Tr[\exp(\mathbf{0})]=2$, the peak of the echo is for $\overline{\mathbf{M}}(0)=\mathbf{1k}$

$$[\overline{M}_y(t')]_n=D_n.\tag{20}$$

Formula (20) is a rigorous proof of a result published previously.[2] This result may be generalized using the method just illustrated to the case where $\mathbf{M}(\Delta\omega)$ is permitted to rotate about the z-axis during all pulses except the two 90°-pulses. The result is that (16) and (18) still hold but $\mathbf{D}_n$ in (18) is now a function of $\Delta\omega$ and the matrix $\boldsymbol{\sigma}_z$;

$$\mathbf{D}_n(\Delta\omega,\boldsymbol{\sigma}_z)=\mathbf{SC}(\mathbf{C}^2)^{n-1}(\mathbf{CC}^*-\mathbf{S}^2)^{N-n},\tag{21}$$

$$\text{where now}\quad\mathbf{C}\equiv\mathbf{1}\cdot\cos(\theta_p/2)-in_z\sin(\theta_p/2)\cdot\boldsymbol{\sigma}_z,\tag{22}$$

and $\mathbf{S}=\mathbf{1}\cdot n_x\sin(\theta_p/2)$, (23)

in which $\theta_p=bt_p$.

The quantities n_x, n_z, and b are functions of $\Delta\omega$, and are given by Bloom.[5] The trace of $\mathbf{D}_n(\Delta\omega,\boldsymbol{\sigma}_z)\exp(i\boldsymbol{\sigma}_z\Delta\omega\tau)$ in (18) may be found in terms of a variable σ_z which takes on the values $+1$ and -1, the diagonal elements of $\boldsymbol{\sigma}_z$. Thus if $D_n(\Delta\omega,\sigma_z)$ be the function

$$D_n(\Delta\omega,\sigma_z)\equiv SC(C^2)^{n-1}(CC^*-S^2)^{N-n}, \tag{24}$$

where $C\equiv\cos(\theta_p/2)-in_z\sin(\theta_p/2)\sigma_z$, (25)

and $S\equiv n_x\sin(\theta_p/2)$, (26)

it follows from the multiplication rule for the diagonal matrices $\mathbf{D}_n$ and $\mathbf{D}_n\exp(i\boldsymbol{\sigma}_z\Delta\omega\tau)$ that

$$Tr[\mathbf{D}_n(\Delta\omega,\boldsymbol{\sigma}_z)\exp(i\boldsymbol{\sigma}_z\Delta\omega\tau)]=D_n(\Delta\omega,+1)\exp(i\Delta\omega\tau)$$

$$+D_n(\Delta\omega,-1)\exp(-i\Delta\omega\tau). \tag{27}$$

By a slight extension of the methods outlined here, $\mathbf{D}_n$ in (16) and (18) may be obtained for the still more general case in which rotation about the z-axis during all pulses except the two 90°-pulses is permitted, and the pulse train consists of pulses of arbitrary amplitude and duration. The result for $\mathbf{D}_n$ is that

$$\mathbf{D}_n(\Delta\omega,\boldsymbol{\sigma}_z)=\mathbf{S}_n\mathbf{C}_n\prod_{i=1}^{i=n-1}(\mathbf{C}_i^2)\cdot\prod_{j=n+1}^{j=N}(\mathbf{C}_j\mathbf{C}_j^*-\mathbf{S}_j^2), \tag{28}$$

where the subscripts n, i, and j indicate that formulas (22) and (23) are to be written for the nth, ith, and jth pulses, respectively. The general result (28) can be expressed in words as follows: The apparent action of each pulse preceding the nth pulse is to multiply $\mathbf{D}_n$ by the factor $\mathbf{C}^2$, and that of every subsequent pulse is to multiply $\mathbf{D}_n$ by $(\mathbf{CC}^*-\mathbf{S}^2)$; the nth pulse itself introduces the factor $\mathbf{SC}$ into $\mathbf{D}_n$.

It may be shown also by this method that the amplitudes of echoes in a train of "inverse order mirror echoes"[2] are twice as large but otherwise identical with those which would be produced in direct order by an "associated pulse train." The associated train is defined as follows: Let the pulse train producing mirror echoes be labelled backwards in time from the 180° pulse as $n=1, 2 \ldots N$; then the "associated pulse train" consists of these same pulses labelled $n=1, 2 \ldots N$ (and the intervals between them) but applied in direct order of time sequence following the first 90°-pulse. The amplitude result follows when $M_y(\Delta\omega)$ is expressed in terms of matrices; the form is almost that of (16). Details of this theory will be published subsequently.

[5] A. L. Bloom, Phys. Rev., **98**, 1105 (1955).

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