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Multipole N.M.R.
III. Multiplet spin theory

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In selective multiquantum N.M.R. specific transitions in the $(2I+1)$ manifold of levels are excited. In order to treat this problem the concept of multiplet spin I_M is introduced which takes all groups of *closest* $(2I_M+1)$ multiplets out of the $(2I+1)$ levels. The theory of multiplet spin is developed and related to the fictitious spin-$\frac{1}{2}$ formalism and the multipole approach.

1. INTRODUCTION

Developments in N.M.R. now permit selective excitation within the manifold of levels available to a spin system. Single, double and higher multiquantum transitions [1] in both single and groups of interacting spins can be observed. These processes are described by the total spin density matrix σ_I even though the N.M.R. technique can directly detect only one part of σ_I which corresponds to the single quantum processes associated with the nuclear magnetic vector. This paper treats single spin systems and describes the multipole operator formalism with selective multiquantum processes in mind.

In developing the theory of pulses on single spins [2] a new way of viewing the spin density matrix has been found which is based upon groupings of closest lines into multiplets. All single levels define multiplet spins of zero ; all pairs of nearest levels define multiplet spins of magnitude $I_M=1/2$; all nearest triplets have $I_M=1$, etc. This construction is found to be useful in describing selective excitation within specific multiplets. The $I_M=|q|/2$ multiplet spin is appropriate for describing the qth quantum processes. In this paper we describe the theory of multiplet spin which is used in later publications to discuss selective multiquantum excitation [3].

The theory of multiplet spin is different from the composite spin construction of spin I and from the fictitious spin-1/2 formulation [4, 5, 6]. The latter takes all *pairs* of levels, rather than groups of *closest* levels, to generate an operator basis.

Fundamental to the approach here is the use of nuclear multipole operators [7–9] to describe the spin density operator. This approach is reviewed in § 3 after spin representation is discussed (§ 2). Section 4 describes the fictitious spin-1/2 formalism and establishes the relation to the multipole approach. The theory of multiplet spin is introduced in § 5 which is followed by some examples and properties.

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2. Spin representation

In this section the basic foundation of spin representation is reviewed. Upon this the multipole, fictitious and various other bases rest. In his work on density matrices, Fano [7] wrote the spin density operator for a spin $I=1/2$ as

$$\sigma_{1/2}=\tfrac{1}{2}(\mathbf{E}_{1/2}+\mathbf{P}\cdot\mathbf{I}). \tag{1}$$

The spin vector polarization is $\mathbf{P}$ and $\mathbf{I}=(I_x, I_y, I_z)$ obeys the commutation relations

$$[I_\alpha, I_\beta]_-=iI_\gamma \tag{2}$$

where $(\alpha\beta\gamma)$ are a cyclic permutation of (xyz). For a spin-1/2 (1) is sufficient since the four operators, the identity $E_{1/2}$, and I_x, I_y and I_z, completely span the operator space. The expectation value of any spin 1/2 operator A is given by the trace with $\sigma_{1/2}$

$$\langle A\rangle=\mathrm{Tr}\,(A\sigma_{1/2}) \tag{3}$$

but knowledge of the vector polarization $\mathbf{P}$ gives complete information about the physical system.

As the spin magnitude increases, more states are available to it there being $(2I+1)^2$ basis operators for spin I of which one is the identity. For spin I the density operator is generalized from (1) to

$$\sigma_I=\sum_{i=1}^{(2I+1)^2} P_iT^i \tag{4}$$

where P_i are the various polarizations and T^i denotes the operator basis. In this paper the primary aim is to study various single spin operator bases T_i.

A convenient operator basis simplifies calculations and has physically useful properties. Ideally, besides being orthonormal with easily calculable commutation relations, the basis should be flexible enough to be applicable to any spin magnitude as well as reflecting as closely as possible the symmetry properties of the spin hamiltonian.

All angular momentum operator bases can be constructed from the two-state spin-1/2 case, these being referred to as $|1\rangle$ and $|2\rangle$. It then follows that four operators, representable as 2×2 matrices, completely span the space and are given by the identity

$$E^{12}=(|1\rangle\langle 1|+|2\rangle\langle 2|) \tag{5}$$

and

$$I_x{}^{12}=\tfrac{1}{2}(|1\rangle\langle 2|+|2\rangle\langle 1|)=\tfrac{1}{2}\sigma_x, \tag{6}$$

$$I_y{}^{12}=\frac{-i}{2}(|1\rangle\langle 2|-|2\rangle\langle 1|)=\tfrac{1}{2}\sigma_y, \tag{7}$$

$$I_z{}^{12}=\tfrac{1}{2}(|1\rangle\langle 1|-|2\rangle\langle 2|)=\tfrac{1}{2}\sigma_z. \tag{8}$$

The identification is made in equations (6–8) with the Pauli spin matrices σ_p.

In summary, the commutative algebra of $I_p{}^{12}$ for a spin 1/2 is su(2) which generates the spinor group SU(2). Equations (5–8) are the starting point for the construction of spin operators which span $(2I+1)\times(2I+1)$ operator space. Two approaches are discussed in turn, namely the multipole basis and the fictitious spin 1/2 basis before discussing the multiplet spin construction.

3. MULTIPOLE BASIS $T^i = \mathscr{I}^{(k)q}$

Traditionally [10] the spin hamiltonian appropriate for N.M.R. is written in terms of tensors which are irreducible under the rotation group. Moreover, the high magnetic fields used mean that the Zeeman term, $\mathbf{I} \cdot \boldsymbol{\alpha}$, usually dominates and the system evolves predominantly as $\exp[-i\mathbf{I} \cdot \boldsymbol{\alpha} t]$. This is recognized as a rotation operator in 3-space [8]. In contrast to using tensors to describe the hamiltonian, it has not been common practice to construct the spin basis in terms of operators which are irreducible under rotations, although some examples exist [11–16]. In the multipole formalism, however, the basis operators are deliberately chosen to be invariant under the rotation group SO(3) in order to exploit the concomitant properties, to provide new physical insight and to ease the labour in calculations, especially for higher spin systems.

To construct this basis we start from a spin 1/2, the SU(2) group. Conveniently SU(2) is homomorphic to SO(3) so this task is simplified (see [8] and references therein). Consequently Racah algebra and Clebsch–Gordan (C–G) coupling can be used in constructing the basis.

The 3 states of $I=1$, for example, can be generated from the two states of 2 composite spins of 1/2, by C–G coupling and higher spin states are obtained by repeating the process. The multipole *operator* basis [9], $T^i = \mathscr{I}^{(k)q}$, is constructed in the same way starting from the Pauli spin matrices. Introducing a spherical basis namely

$$e^{(1)0} = iz,\ e^{(1)1\pm1} = \mp\frac{i}{\sqrt{2}}(x \pm iy) \tag{9}$$

the three operators for $I=1/2$ are

$$\mathscr{I}^{(1)0}(\mathbf{I}) = i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\sigma_z, \tag{10}$$

$$\mathscr{I}^{(1)1}(\mathbf{I}) = -i\sqrt{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \frac{-i}{\sqrt{2}}(\sigma_x + i\sigma_y), \tag{11}$$

$$\mathscr{I}^{(1)-1}(\mathbf{I}) = i\sqrt{2}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \frac{i}{\sqrt{2}}(\sigma_x - i\sigma_y), \tag{12}$$

with both matrix and Pauli spin operators relationships given. In this basis the spherical components $q=0,\ \pm1$ corresponds to a transition $|M\rangle\langle M-q|$. It is remarked that the imaginary prefactor in the spherical basis (9) is a matter of personal choice and does not affect the final results. Another popular basis, namely $e^{(1)0} = z$ and $e^{(1)\pm1} = \mp 1/\sqrt{2}(x \pm iy)$ only introduces a phase difference.

By repeated C–G coupling of $\mathscr{I}^{(1)q}$ operator for a spin 1/2, spherical tensor components $\mathscr{I}^{(k)q}(\mathbf{I})$ can be constructed for spin I. Relating the $\mathscr{I}^{(k)q}(\mathbf{I})$ to the $|IM\rangle\langle IM'|$ operator basis gives a representation for the $\mathscr{I}^{(k)q}$s for any I as [9]

$$\mathscr{I}^{(k)q}(\mathbf{I}) = (i)^k[(2I+1)(2k+1)]^{1/2}\sum_{MM'}(-1)^{I-M} \times \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix}|IM\rangle\langle IM'|. \tag{13}$$

Table 1. Representation of $\mathscr{Y}^{(k)q}(\mathbf{I})$ in the $|IM\rangle\langle IM'|$ basis for $I=1/2$ to $I=5/2$. The relation $\mathscr{Y}^{(k)q^{*t}}(\mathbf{I})=(-1)^{k-q}\mathscr{Y}^{(k)-q}(\mathbf{I})$, where t is matrix transpose and * is complex conjugation, can be used to obtain $\mathscr{Y}^{(k)-q}(\mathbf{I})$.

$I=1/2$

$$\mathscr{Y}^{(1)0}=i\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} \qquad \mathscr{Y}^{(1)1}=-i\sqrt{2}\begin{bmatrix}0 & 1\\ 0 & 0\end{bmatrix}$$

$I=1$

$$\mathscr{Y}^{(1)0}=i\sqrt{\tfrac{3}{2}}\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix} \qquad \mathscr{Y}^{(1)1}=-i\sqrt{\tfrac{3}{2}}\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 0 & 0 & 0\end{bmatrix}$$

$$\mathscr{Y}^{(2)0}=\frac{1}{\sqrt{2}}\begin{bmatrix}-1 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & -1\end{bmatrix} \qquad \mathscr{Y}^{(2)1}=\sqrt{\tfrac{3}{2}}\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & -1\\ 0 & 0 & 0\end{bmatrix}$$

$$\mathscr{Y}^{(2)2}=\sqrt{3}\begin{bmatrix}0 & 0 & -1\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix}$$

$I=3/2$

$$\mathscr{Y}^{(1)0}=\frac{i}{\sqrt{5}}\begin{bmatrix}3 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -3\end{bmatrix} \qquad \mathscr{Y}^{(1)1}=-i\sqrt{\tfrac{6}{5}}\begin{bmatrix}0 & 1 & 0 & 0\\ 0 & 0 & 2/\sqrt{3} & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{bmatrix}$$

$$\mathscr{Y}^{(2)0}=\begin{bmatrix}-1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\end{bmatrix} \qquad \mathscr{Y}^{(2)1}=-\sqrt{2}\begin{bmatrix}0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{bmatrix}$$

$$\mathscr{Y}^{(2)2}=-\sqrt{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{bmatrix}$$

$$\mathscr{Y}^{(3)0}=\frac{i}{\sqrt{5}}\begin{bmatrix}-1 & 0 & 0 & 0\\ 0 & 3 & 0 & 0\\ 0 & 0 & -3 & 0\\ 0 & 0 & 0 & 1\end{bmatrix} \qquad \mathscr{Y}^{(3)1}=\frac{i2}{\sqrt{5}}\begin{bmatrix}0 & 1 & 0 & 0\\ 0 & 0 & -\sqrt{3} & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0\end{bmatrix}$$

Table 1 (*continued*)

$I=3/2$

$$\mathscr{J}^{(3)2}=i\sqrt{2}\begin{bmatrix}0&0&-1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{bmatrix}\qquad \mathscr{J}^{(3)3}=i\begin{bmatrix}0&0&0&2\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{bmatrix}$$

$I=2$

$$\mathscr{J}^{(1)0}=\frac{i}{\sqrt{2}}\begin{bmatrix}2&0&0&0&0\\0&1&0&0&0\\0&0&0&0&0\\0&0&0&-1&0\\0&0&0&0&-2\end{bmatrix}\qquad \mathscr{J}^{(1)1}=-i\begin{bmatrix}0&1&0&0&0\\0&0&\sqrt{(3/2)}&0&0\\0&0&0&\sqrt{(3/2)}&0\\0&0&0&0&1\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{J}^{(2)0}=-\sqrt{\tfrac{5}{14}}\begin{bmatrix}2&0&0&0&0\\0&-1&0&0&0\\0&0&-2&0&0\\0&0&0&-1&0\\0&0&0&0&2\end{bmatrix}\qquad \mathscr{J}^{(2)1}=\sqrt{\tfrac{5}{14}}\begin{bmatrix}0&\sqrt{6}&0&0&0\\0&0&1&0&0\\0&0&0&-1&0\\0&0&0&0&\sqrt{6}\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{J}^{(2)2}=-\sqrt{\tfrac{5}{14}}\begin{bmatrix}0&0&2&0&0\\0&0&0&\sqrt{6}&0\\0&0&0&0&2\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{J}^{(3)0}=\frac{-i}{\sqrt{2}}\begin{bmatrix}1&0&0&0&0\\0&-2&0&0&0\\0&0&0&0&0\\0&0&0&2&0\\0&0&0&0&-1\end{bmatrix}\qquad \mathscr{J}^{(3)1}=-i\begin{bmatrix}0&-\sqrt{(3/2)}&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&-\sqrt{(3/2)}\\0&0&0&0&0\end{bmatrix}$$

Table 1 (*continued*)

$I=2$

$$\mathscr{Y}^{(3)2}=-i\sqrt{\tfrac{5}{2}}\begin{bmatrix}0&0&1&0&0\\0&0&0&0&0\\0&0&0&0&-1\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}\qquad \mathscr{Y}^{(3)3}=+i\sqrt{\tfrac{5}{2}}\begin{bmatrix}0&0&0&1&0\\0&0&0&0&1\\0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{Y}^{(4)0}=\frac{1}{\sqrt{(14)}}\begin{bmatrix}4&0&0&0&0\\0&-1&0&0&0\\0&0&6&0&0\\0&0&0&-1&0\\0&0&0&0&4\end{bmatrix}\qquad \mathscr{Y}^{(4)1}=\sqrt{\tfrac{5}{14}}\begin{bmatrix}0&-1&0&0&0\\0&0&\sqrt{6}&0&0\\0&0&0&-\sqrt{6}&0\\0&0&0&0&1\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{Y}^{(4)2}=\sqrt{\tfrac{5}{14}}\begin{bmatrix}0&0&\sqrt{3}&0&0\\0&0&0&-\sqrt{8}&0\\0&0&0&0&\sqrt{3}\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}\qquad \mathscr{Y}^{(4)3}=\sqrt{\tfrac{5}{2}}\begin{bmatrix}0&0&0&-1&0\\0&0&0&0&1\\0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}$$

$$\mathscr{Y}^{(4)4}=\sqrt{5}\begin{bmatrix}0&0&0&0&1\\0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}$$

$I=5/2$

$$\mathscr{Y}^{(1)0}=+i\sqrt{\tfrac{3}{35}}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&-5\end{bmatrix}\qquad \mathscr{Y}^{(1)1}=-i\sqrt{(\tfrac{6}{7})}\begin{bmatrix}0&1&0&0&0&0\\0&0&\sqrt{(8/5)}&0&0&0\\0&0&0&\sqrt{(9/5)}&0&0\\0&0&0&0&\sqrt{(8/5)}&0\\0&0&0&0&0&1\\0&0&0&0&0&0\end{bmatrix}$$

Table 1 (*continued*)

$I = 5/2$

$$\mathcal{J}^{(2)0} = \frac{1}{\sqrt{(14)}} \begin{bmatrix} -5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{bmatrix} \qquad \mathcal{J}^{(2)1} = \sqrt{\tfrac{3}{35}} \begin{bmatrix} 0 & 5 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{(10)} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{(10)} & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathcal{J}^{(2)2} = -\frac{1}{\sqrt{(14)}} \begin{bmatrix} 0 & 0 & \sqrt{15} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{27} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{27} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{15} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \mathcal{J}^{(3)0} = \frac{-i}{\sqrt{(30)}} \begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & -7 & 0 & 0 & 0 & 0 \\ 0 & 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 7 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{bmatrix}$$

$$\mathcal{J}^{(3)1} = \frac{-i}{\sqrt{5}} \begin{bmatrix} 0 & -\sqrt{10} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{8} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{10} \end{bmatrix} \qquad \mathcal{J}^{(3)2} = \frac{-i}{\sqrt{2}} \begin{bmatrix} 0 & 0 & \sqrt{5} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathcal{J}^{(3)3} = \frac{+i}{\sqrt{3}} \begin{bmatrix} 0 & 0 & 0 & \sqrt{5} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{8} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \mathcal{J}^{(4)0} = \sqrt{\tfrac{3}{14}} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\mathcal{J}^{(4)1} = \sqrt{(\tfrac{3}{7})} \begin{bmatrix} 0 & -\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{5} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{5} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} \end{bmatrix} \qquad \mathcal{J}^{(4)2} = \sqrt{\tfrac{3}{14}} \begin{bmatrix} 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{5} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{5} & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Table 1 (*continued*)

$I = 5/2$

$$\mathscr{Y}^{(4)3} = \sqrt{3}\begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \mathscr{Y}^{(4)4} = \sqrt{3}\begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathscr{Y}^{(5)0} = +\frac{i}{\sqrt{(42)}}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 10 & 0 & 0 & 0 \\ 0 & 0 & 0 & -10 & 0 & 0 \\ 0 & 0 & 0 & 0 & 5 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \qquad \mathscr{Y}^{(5)1} = \frac{-i}{\sqrt{7}}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\sqrt{(10)} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{(20)} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{(10)} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathscr{Y}^{(5)2} = +\frac{i}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{5} & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \mathscr{Y}^{(5)3} = \frac{-i}{\sqrt{3}}\begin{bmatrix} 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{(10)} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathscr{Y}^{(5)4} = i\sqrt{3}\begin{bmatrix} 0 & 0 & 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \mathscr{Y}^{(5)5} = i\sqrt{6}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

The equations (10)–(12) are special cases of (13) when $I = 1/2$. Table 1 gives the matrix representations up to $I = 5/2$. These are presented not for use in matrix algebra calculations but rather to display the tensor, or multipole, character of the various $q = \Delta M$ components which are found to be useful in single spin examples (§ 6).

Both k and q take integer values only and it is easy to check that the $\mathscr{I}^{(k)q}$s provide the correct number of $(2I+I)^2$ operators. In fact, the multipole basis is complete and spans the spin space so any operator can be expressed as a linear combination of its $\mathscr{I}^{(k)q}$s. In particular the spin density operator is

$$\sigma_I(t)=\frac{1}{2I+1}\left[E_I+\sum_{k=1}^{2I}\sum_{q=-k}^{k}\mathscr{I}^{(k)q}(\mathbf{I})\phi_q{}^k(t)\right], \tag{14}$$

where the polarization $\phi_q{}^k(t)$ are time dependent. Treating the density operator as time dependent in (3) is the Schrodinger picture. The inverse of (13) is [9]

$$|IM\rangle\langle IM'|=(2I+1)^{-1/2}(-1)^{I-M}\sum_{k=0}^{2I}\sum_{q=-k}^{k}(2k+1)^{1/2}(-i)^k \times\begin{pmatrix} I & k & I \\ -M & q & M'\end{pmatrix}\mathscr{I}^{(k)q}(\mathbf{I}), \tag{15}$$

which is the multipole expansion for the operator $|IM\rangle\langle IM'|$.

Constructed in this way, the multipoles $\mathscr{I}^{(k)}(\mathbf{I})$ are kth rank tensors irreducible under the rotation group. The spherical component q denotes all contributions from the qth quantum coherence $q=M-M'$.

A summary of the most useful properties of the $\mathscr{I}^{(k)q}$s follows [9].

(i) operator adjoint

$$\mathscr{I}^{(k)q\dagger}(\mathbf{I})=(-1)^{k-q}\mathscr{I}^{k-q}(\mathbf{I})\equiv\mathscr{I}_q{}^{(k)}(\mathbf{I}). \tag{16}$$

In matrix form, table 1, the adjoint is complex conjugation and matrix transpose,

(ii) orthonormalization and inner product,

$$\langle\!\langle\,\mathscr{I}^{(k)q}|\,\mathscr{I}^{(k')q'}\rangle\!\rangle\equiv\mathrm{Tr}\;\mathscr{I}^{(k)q}(\mathbf{I})^\dagger\mathscr{I}^{(k')q'}(\mathbf{I}) =\delta_{kk'}\delta_{qq'}(2I+1), \tag{17}$$

(iii) matrix elements (Wigner–Eckart theorem)

$$\langle\!\langle\,\mathscr{I}^{(k)q}|\,\mathscr{I}^{(l)m}|\,\mathscr{I}^{(k')q'}\rangle\!\rangle=(-1)^{k-q}\begin{Bmatrix} k & l & k' \\ -q & m & q'\end{Bmatrix}\langle\!\langle\,\mathscr{I}^{(k)}\|\,\mathscr{I}^{(l)}\|\,\mathscr{I}^{(k')}\rangle\!\rangle, \tag{18}$$

where the reduced matrix element is

$$\langle\!\langle\,\mathscr{I}^{(k)}\|\,\mathscr{I}^{(l)}\|\,\mathscr{I}^{(k')}\rangle\!\rangle=(i)^{k'+l+k}[(2l+1)(2k+1)(2I+1)]^{1/2} \times(-1)^{2I}\begin{pmatrix} I & I & k' \\ l & k & I\end{pmatrix}(2I+1)(-1)^{l-k'+k}(2k'+1)^{1/2}, \tag{19}$$

where $\begin{Bmatrix}\cdots\\ \cdots\end{Bmatrix}$ is a 6-j coefficient [8].

(iv) commutation relation [9]

$$[\mathscr{I}(\mathbf{I})^{(l)m},\mathscr{I}(\mathbf{I})^{(k)q}]_-=2\sum_{k'q'}\phi(klk')\langle\!\langle\,\mathscr{I}^{(k')q'}|\,\mathscr{I}^{(l)m}|\,\mathscr{I}^{(k)q}\rangle\!\rangle\,\mathscr{I}^{(k')q'}(\mathbf{I}), \tag{20}$$

where $\phi(l_1l_2l_3)$ is one if $l_1+l_2+l_3$ is odd and zero if even. Table 2 relates the $\mathscr{I}^{(k)q}$s to I_z, $I_x\pm iI_y$ for $k\leqslant 3$.

Table 2. Relation of $\mathscr{Y}^{(k)q}(I)$ to I_z and $I_\pm = I_x \pm iI_y$ operators up to $k=3$.

k	q	$\mathscr{Y}^{(k)q}(I)$
0	0	1
1	0	$\{3/I(I+1)\}^{1/2}\, i(I_z)$
1	± 1	$\{3/I(I+1)\}^{1/2}(\mp i/\sqrt{2})(I_\pm)$
2	0	$\{5/[\mathbf{I}]^{(2)} : [\mathbf{I}]^{(2)}\}^{1/2}(1/\sqrt{6})(I^2 - 3I_z^2)$
2	± 1	$\{5/[\mathbf{I}]^{(2)} : [\mathbf{I}]^{(2)}\}^{1/2}(\pm 1/2)(I_zI_\pm + I_\pm I_z)$
2	± 2	$\{5/[\mathbf{I}]^{(2)} : [\mathbf{I}]^{(2)}\}^{1/2}(-1/2)(I_\pm I_\pm)$
3	0	$\{7/[\mathbf{I}]^{(3)} : [\mathbf{I}]^{(3)}\}^{1/2}(i/\sqrt{(10)})(3I^2 - 5I_z^2 - 1)I_z$
3	± 1	$\{7/[\mathbf{I}]^{(3)} : [\mathbf{I}]^{(3)}\}^{1/2}[(\pm i\sqrt{[3/10]})/4]\{I_\pm(I^2 - 5I_z + 1/2) + (I^2 - 5I_z + 1/2)I_\pm\}$
3	± 2	$\{7/[\mathbf{I}]^{(3)} : [\mathbf{I}]^{(3)}\}^{1/2}(-i\sqrt{3}/2)(I_\pm I_z I_\pm)$
3	± 3	$\{7/[\mathbf{I}]^{(3)} : [\mathbf{I}]^{(3)}\}^{1/2}(\pm i/2\sqrt{2})I_\pm I_\pm I_\pm$

$$[\mathbf{I}]^{(k)} \bigcirc^k [\mathbf{I}]^{(k)} = \frac{(k!)^2(2I+k+1)!}{2^k(2I+1)(2k)!(2I-k)!}$$

The use of spherical tensor operators in N.M.R. is not new. It is, of course, common practice to express the hamiltonian in terms of tensor operators for the spin and lattice parts. It is not as common to apply the same construction to the operator basis, $|IM\rangle\langle IM'|$ although this approach was perhaps first used in N.M.R. by Banwell and Primas [17]. They used the Liouville formulation to directly calculate the frequency spectra rather than obtaining the energy levels first. They also introduced rotationally invariant spin operators for mathematical convenience. Subsequent applications appear mainly motivated by the mathematical advantages of tensor operators with Pyper [14], Lynden-Bell [15] and Bain [13] showing how relaxation effects can be handled quite generally and include treatments of several coupled spins. Spiess [11, 18] and Fedders [12] use the multipole construction and apply the results to respectively solids and nuclear acoustic resonance. Chen and Snider [19] have applied irreducible tensors to N.M.R. of gases. The notation, phase convention and construction of the operators $\mathscr{Y}^{(k)q}(\mathbf{I})$ comes from a series of papers by Coope *et al.* [20]. Theory and applications to spin dynamics and relaxation have been treated by the author [2, 3, 9, 25].

The main difference between the approach used in the present series and previous work lies in the way the multipole operators are physically exploited. The expectation values of the higher multipoles are observables and describe multiquantum processes, 2-D spectroscopy and coherence transfer experiments. Rather than discuss a process as either a population or an off-diagonal element of the spin density matrix, we prefer to discuss the multipole character of the quantity under study. Consequently, in addition to the mathematical advantages, the physical content of the operator basis is considered important. Thus, from equation (14), $\phi_0{}^1$ is the z component of the nuclear magnetization; $\phi_{\pm 1}{}^1$ are detected in normal N.M.R; $\phi_{\pm 1}{}^2$ is observed in nuclear acoustic

resonance [12]; $\phi_0{}^2$ is studied by the Jeener–Brockaert pulse sequence [26]; $\phi_{\pm 2}{}^2$ describes the quadrupole contribution to double quantum processes etc.

Clearly the nuclear spin has no classical limit. If, however, **I** is replaced by a classical vector with angles θ and ϕ, the multipole operators become spherical harmonics,

$$\mathscr{T}^{(k)q}(\mathbf{I}) \to (i)^k \sqrt{(4\pi)}\, Y_{kq}(\theta\phi) \tag{21}$$

4. Fictitious spin basis $T^i = I_p{}^{rs}$

The representation of a spin 1/2 by the Pauli spin matrices, equations (6–8) can be extended to higher spins as follows. For $I=1$ the three states are denoted by $|1\rangle$, $|2\rangle$ and $|3\rangle$. It is possible to generate 9, 2×2 Pauli spin matrices by taking all pairs rs, r, $s=1$, 3 with $r<s$, namely

$$I_p{}^{12},\ I_p{}^{13},\ I_p{}^{23} \quad p=x, y, z. \tag{22}$$

For $I=3/2$, the 4 states generate 18, 2×2 matrices

$$I_p{}^{12},\ I_p{}^{13},\ I_p{}^{14},\ I_p{}^{23},\ I_p{}^{24},\ I_p{}^{34}. \tag{23}$$

Vega and Pines [4] call the generation of the various $I_p{}^{rs}$ for higher spins ' fictitious ' spins 1/2 after Abragam [10] because they all have the Pauli spin 2×2 structure and obey

$$[I_\alpha{}^{rs},\ I_\beta{}^{rs}]_- = iI_\gamma{}^{rs} \tag{24}$$

for each pair rs. They are in fact 2×2 matrices embedded in matrices of dimension $(2I+1)^2$. On the other hand the commutation relations between $I_p{}^{rs}$ is overcomplete, since from equation (8) for $I_z{}^{rs}$, each pair can be made from two others,

$$I_z{}^{rs} = I_z{}^{1s} - I_z{}^{1r}. \tag{25}$$

Hence the sum

$$I_z{}^{rs} + I_z{}^{st} + I_z{}^{tr} = 0 \tag{26}$$

must vanish showing that the z components are linearly dependent. For $n=2I+1$ states there are $(n-1)(\frac{1}{2}n-1)$ such relations. Consequently the set $I_p{}^{rs}$ along with the relations (26) completely span the spin space.

This method of representing spin is well known in group theory [21] and particle physics [22] especially for SU(3). A particularly physically revealing basis based upon SU(3) is given by Vega and Pines [4] where $I=1$ is depicted in 3 coordinate frames of 3-dimensions each. In other work [5, 6, 23] the $I_p{}^{rs}$ basis is used and Ernst [6] has given the unitary transformation between Vega and Pines [4] basis for $I=1$ and the $I_p{}^{rs}$ basis.

The fictitious spin 1/2 basis, besides being overcomplete, is non-orthogonal. The commutation relations can be calculated quite generally but no single compact expression is found analogous to (20). The appeal of the fictitious spin 1/2 basis lies in separating pairs of levels which then obey the usual spin-1/2 commutation relations (2). If the hamiltonian does not couple other levels to this pair then a simple picture emerges of rotation of spin operators [4, 5, 6, 24] in a coordinate system labelled by $I_p{}^{rs}$ ($p=x$, y and z).

The relation between the fictitious spin-1/2 formalism and the multipole basis can be established. All doublets separated by $\Delta M=q$, see figure 1 (*a*) can be completely described by the 3 fictitious spin-1/2 Pauli operators which,

from (6–8), are

$$2I_x^{rs}=\sigma_x(Mq)=|IM\rangle\langle IM-q|+|IM-q\rangle\langle IM|, \tag{27}$$

$$2I_y^{rs}=\sigma_y(Mq)=-i(|IM\rangle\langle IM-q|-|IM-q\rangle\langle IM|), \tag{28}$$

$$2I_z^{rs}=\sigma_z(Mq)=|IM\rangle\langle IM|-|IM-q\rangle\langle IM-q|. \tag{29}$$

Here r refers to $|IM\rangle$ and s to $|IM-q\rangle$. Using instead the spherical basis, (10)–(12), the fictitious spin-1/2 Pauli spin matrices are, in terms of multipoles (use equation (15)),

$$\sigma_0(Mq)=-i(2I+1)^{-1/2}(-1)^{I-M}\sum_{k=1}^{2I}(2k+1)^{1/2}(-i)^k \times\left[\begin{pmatrix} I & k & I \\ -M & 0 & M\end{pmatrix}-(-)^q\begin{pmatrix} I & k & I \\ -M+q & 0 & M-q\end{pmatrix}\right]\mathcal{T}^{(k)0}(I), \tag{30}$$

$$\left.\begin{matrix}\sigma_{-1}(Mq)\\ \sigma_{+1}(Mq)\end{matrix}\right\}=\sqrt{2}(2I+1)^{-1/2}(-1)^{I-M}\sum_{k=|q|}^{2I}(2k+1)^{1/2} \times\begin{pmatrix} I & k & I \\ -M & q & (M-q)\end{pmatrix}\begin{Bmatrix}(i)^{k+1}\ \mathcal{T}^{(k)q\dagger}\\ (-i)^{k+1}\ \mathcal{T}^{(k)q}\end{Bmatrix} \tag{31}$$

These relate fictitious and multipole operators and lead to table 3 for $I=1$. In matrix notation, fictitious Pauli spin matrices are 2×2 submatrices in $2I+1$ space.

Table 3. Relation between the multipole basis and the fictitious spin-1/2 basis for $I=1$.

$$I_x^{12}=\frac{1}{2\sqrt{6}}[i(\mathcal{T}^{(1)1}-\mathcal{T}^{(1)-1})+(\mathcal{T}^{(2)1}+\mathcal{T}^{(2)-1})]$$

$$I_x^{23}=\frac{1}{2\sqrt{6}}[i(\mathcal{T}^{(1)1}-\mathcal{T}^{(1)-1})-(\mathcal{T}^{(2)1}+\mathcal{T}^{(2)-1}]$$

$$I_x^{13}=-\frac{1}{2\sqrt{3}}[\mathcal{T}^{(2)2}+\mathcal{T}^{(2)-2}]$$

$$I_y^{12}=\frac{1}{2\sqrt{6}}[(\mathcal{T}^{(1)1}+\mathcal{T}^{(1)-1})-i(\mathcal{T}^{(2)1}-\mathcal{T}^{(2)-1})]$$

$$I_y^{23}=\frac{1}{2\sqrt{6}}[(\mathcal{T}^{(1)1}+\mathcal{T}^{(1)-1})+i(\mathcal{T}^{(2)1}-\mathcal{T}^{(2)-1})]$$

$$I_y^{13}=\frac{i}{2\sqrt{3}}[\mathcal{T}^{(2)2}-\mathcal{T}^{(2)-2}]$$

$$I_z^{12}=-\frac{1}{2\sqrt{6}}[\sqrt{3}\mathcal{T}^{(2)0}+i\mathcal{T}^{(1)0}]$$

$$I_z^{23}=\frac{1}{2\sqrt{6}}[\sqrt{3}\mathcal{T}^{(2)0}-i\mathcal{T}^{(1)0}]$$

$$I_z^{13}=-\frac{i}{\sqrt{6}}\mathcal{T}^{(1)0}$$

5. Multiplet spins I_M

Figure 1 shows the four levels of $I=3/2$ labelled both by the M value and the composite spin state, figure 1 (*b*). A non-selective near resonant excitation causes a transition to occur simultaneously between the levels. For $\Delta M=1$, there are three single quantum processes. Similarly two double, $\Delta M=2$, and one triple quantum, $\Delta M=3$, processes can occur. In contrast a selective transition, possible by virtue of unequal level splittings, can be made to produce a transition in only one of the six possible multiquantum processes.

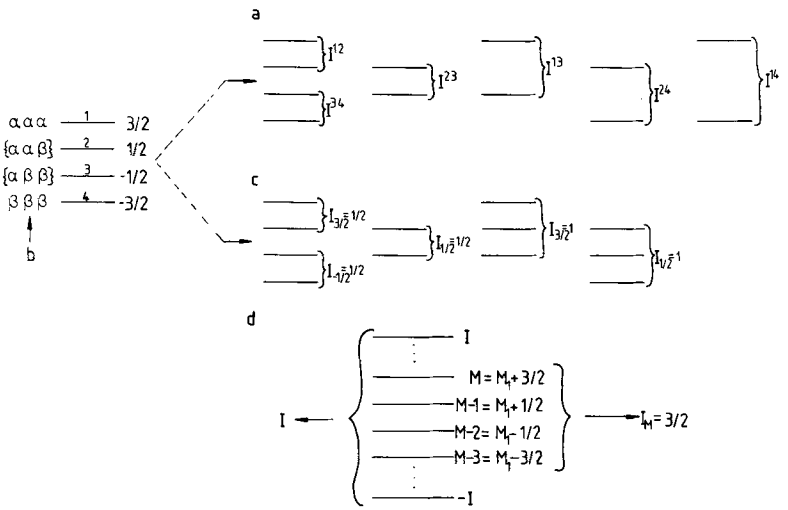

Figure 1. (*a*) Fictitious spin-1/2 decomposition for $I=3/2$—all doublets. (*b*) Composite spin-1/2 structure for spin $I=3/2$. (*c*) Multiplet spin decomposition for $I=3/2$—all nearest multiplets. (*d*) Multiplet spin $I_M=3/2$ defined in a $(2I+1)$ manifold of a spin I from levels M to $M-3$.

The fictitious spin formalism, figure 1 (*a*), picks out the appropriate *pair* of levels excited. The multiplet spin approach includes also the levels *in between* the initial and final states (figure 1 (*c*)).

There are two main reasons for defining a multiplet spin in this manner. All multiquantum processes, even $|\Delta M|>1$, occur by multiple single quantum jumps of ± 1. It is physically and mathematically reasonable to include not only the initial and final states, but also the states in between to accommodate the ± 1 jumps. For delta function pulses, furthermore, the simple vector rotation model of usual N.M.R. can be extended to selective single and multiquantum processes. That is, the picture of rotating the magnetic vector carries over exactly to the selective cases, but for a multiplet spin rather than the total spin.

These features arise because the multiplet of levels excited in selective processes can be treated as an uncoupled multiplet within the total I manifold. Hence the multiplet spin admits its own operator basis and can be treated by standard spin angular momentum methods.

In the remainder of this section multiplet spins and some of their properties are defined mathematically. Section 6 discusses some physical aspects.

5.1. *Multiplet spin* 1/2

Taking groups of closest doublets, the Pauli spin 1/2 matrices, equations (30)–(31) are written,

$$\mathscr{y}_{1/2}{}^{(1)q}(M) \equiv \sigma_q(M1). \tag{32}$$

This definition is used only for $|q| \leqslant 1$. The sets of operators for $I_M = 1/2$ each have the 2×2 structure as for $I = 1/2$ in table 1, but embedded in $2I+1$ space. Operators $\mathscr{y}_{1/2}{}^{(1)q}(M)$ are useful for treating single quantum processes. For a spin I there are $2I$ sets of multiplet spin 1/2 operators namely $\mathscr{y}_{1/2}{}^{(1)q}(I)$, $\mathscr{y}_{1/2}{}^{(1)q}(I-1) \ldots \mathscr{y}_{1/2}{}^{(1)q}(-I+1)$.

5.2. *Higher multiplet spins*

All nearest groups of triplets are described by $\mathscr{y}_1{}^{(l)q}(M)$, $l = 0, 1, 2$ and all nearest groups of $(2I_M+1)$ multiplets are described by $\mathscr{y}_{I_M}{}^{(l)q}(M)$ $(I_M < I)$, $0 < l \leqslant 2I_M$.

Each of these multiplet spin operators has the $(2I_M+1)$ structure of spin $I = I_M$ in table 1, embedded in the larger total spin space. All properties of $\mathscr{y}_{I_M}{}^{(l)q}(M)$ are the same as $\mathscr{y}^{(l)q}(\mathbf{I})$, i.e. the same as (15)–(20). The difference lies in that each $\mathscr{y}_{I_M}{}^{(l)q}(M)$ is a submatrix of the corresponding set $\mathscr{y}^{(k)q}(\mathbf{I})$ which starts at level M and includes only the $2I_M$ multiplet of levels below it. However different multiplet spins do not commute.

5.3. *Multiplet basis*

A multiplet spin basis can be written $|I_M M_1 + M_M\rangle\langle I_M M_1 + M'_M|$ where M_1 is defined by

$$M_1 = M - I_M. \tag{33}$$

Figure 1 (*d*) illustrates this for an arbitrary manifold. Consider a multiplet spin $I_M = 3/2$ in a $2I+1$ spin system. Starting at level M select the 3 levels below where $M_1 = M - 3/2$ with the restriction,

$$I > 2I_M - M. \tag{34}$$

These four levels describe a multiplet spin $I_M = 3/2$ for levels M to M–3.

5.4. *Relation to multipole operators*

The relation between the multiplet spin operator basis $\mathscr{y}_{I_M}{}^{(l)q}(M)$ and the full spin operator basis $\mathscr{y}^{(k)q}(\mathbf{I})$ is found by using equation (13) for $\mathscr{y}_{I_M}{}^{(l)}$. After noting that $|I_M M_1 + M_M\rangle = |IM\rangle$, (15) can be used to give

$$\begin{aligned}\mathscr{y}_{I_M}{}^{(l)q}(M) = \sum_{M_M M'_M}^{k} (i)^{l-k} \left[\frac{(2I_M+1)}{(2I+1)}(2l+1)(2k+1)\right]^{1/2} \\ \times (-1)^{I-M+I_M-M_M} \begin{pmatrix} I_M & l & I_M \\ -M_M & q & M'_M \end{pmatrix} \\ \times \begin{pmatrix} I & k & I \\ -(M_1+M_M) & q & (M_1+M'_M) \end{pmatrix} \mathscr{y}^{(k)q}(\mathbf{I}).\end{aligned} \tag{35}$$

In the special case when $I = I_M$ it follows that $M_1 = 0$ and $M = M_M$ so the multiplet spin operator becomes the full spin I operator as expected.

5.5. *Relation of multipoles to multiplet operators*

The inverse of equation (35) can also be given. One form is

$$\mathscr{I}^{(k)q}(\mathbf{I}) = i^k \sqrt{\left[\frac{(2I+1)(2k+1)}{(2I_M+1)}\right]} \sum_{\substack{M_1 M_M M'_M \\ p}} (-1)^{I+I_M-M-M_M} \sqrt{(2p+1)}(-i)^p \times \begin{pmatrix} I & k & I \\ -M_1-M_M & q & M_1+M'_M \end{pmatrix} \begin{pmatrix} I_M & p & I_M \\ -M_M & qM'_M \end{pmatrix} \mathscr{I}_{I_M}{}^{(p)q}(M) \quad (36)$$

and for fixed I_M the decomposition is unique. That is there is one multiplet spin decomposition namely $I_M \geq |q/2|$ which generates all $\mathscr{I}^{(k)q}(\mathbf{I})$ for any I. It is also possible to decompose $\mathscr{I}^{(k)q}$ with multiplet spins of different magnitude by relating $\mathscr{I}_{I_M}{}^{(p)q}(M)$ in (36) to other $\mathscr{I}_{I_{M'}}{}^{(l)q}(M_M)$ using (35). This construction is not unique and the general formulae become tedious to use. In § 6 a method is introduced, however, for extracting the relevant multiplet spin density operator from the total spin density operator which circumvents the Clebsch–Gordan algebra.

5.6. *Multiplet spin of zero*

For a single spin system of spin I, the Mth multiplet spin of zero describes the population of the Mth level. All $\mathscr{I}^{(k)0}(\mathbf{I})$ with $q = 0$ can be generated by the $2I+1$ multiplet spins of zero for which there is only one basis operator namely the identity,

$$\mathscr{I}_0{}^{(0)0}(M) = |IM\rangle\langle IM|. \quad (37)$$

This gives simply

$$\mathscr{I}^{(k)0}(I) = i^k \sqrt{[(2I+1)(2k+1)]} \sum_M (-1)^{I-M} \begin{pmatrix} I & k & I \\ -M & 0 & M \end{pmatrix} \mathscr{I}_0{}^{(0)0}(M). \quad (38)$$

The identity operator for $I_M = 0$ is a diagonal matrix with one element non-zero.

$$\mathscr{I}_0{}^{(0)0}(M) = |IM\rangle \begin{bmatrix} \langle IM| & & & & & \\ 0 & & & & & \\ & \ddots & & & & \\ & & 1 & & & \\ & & & \ddots & & \\ & & & & 0 & \\ & & & & & 0 \\ & & & & & & 0 \end{bmatrix} \quad (39)$$

In terms of an equilibrium density operator, the $\mathscr{I}^{(k)0}(\mathbf{I})$ give the energy level splitting. For $I = 1$ and $I = 3/2$ the expressions are, (cf. equation (14))

$$\sigma_1 = \tfrac{1}{3}\,[E_1 + \phi_0{}^1\ \mathscr{I}^{(1)0} + \phi_0{}^2\ \mathscr{I}^{(2)0}] \quad (40)$$

and

$$\sigma_{3/2} = \tfrac{1}{4}\,[E_{3/2} + \phi_0{}^1\ \mathscr{I}^{(1)0} + \phi_0{}^2\ \mathscr{I}^{(2)0} + \phi_0{}^3\ \mathscr{I}^{(3)0}]. \quad (41)$$

Usually $\phi_0{}^1$, which is proportional to the nuclear magnetization ($\phi_0{}^1 \propto \hbar\omega_0/kT$), dominates the quadrupole and octupole, etc., polarization in a vector magnetic field along the z direction. Figure 2 shows some types of splittings described by $\mathscr{y}^{(k)0}$ for $I=1$ and 3/2.

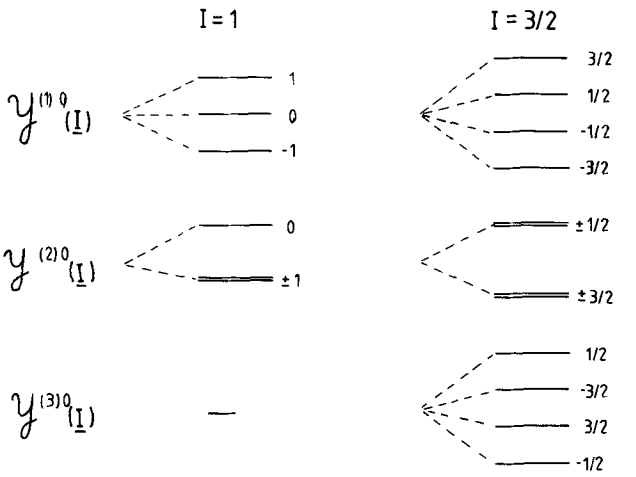

Figure 2. Energy level structure arising from the diagonal multipoles for spins $I=1$ and 3/2.

5.7. *Multiplet spin* 1/2 *weights*

Of particular importance in N.M.R. is the vector operator $\mathscr{y}^{(1)\pm1}(\mathbf{I})$ which is proportional to the raising and lowering operators. Among others these arise in the rf part of the hamiltonian. The multiplet spin 1/2 is related to $\mathscr{y}^{(1)\pm1}$ by

$$\mathscr{y}^{(1)\pm1}(I)=\frac{1}{\sqrt{2}}\sqrt{\left[\frac{3}{I(I+1)}\right]}\sum_M \sqrt{[(I+M)(I-M+1)]}\,\mathscr{y}_{1/2}{}^{(1)\pm1}(M) \qquad (42)$$

which shows that decomposition of the vector operator into $I_M=1/2$, weights each multiplet spin differently. For $I=1$ and $\frac{3}{2}$, (42) is the origin of the $\sqrt{2}$ and $\sqrt{3}$ factors which are found in the fictitious spin 1/2 approach [4, 5, 6]. Removing the normalization of the $\mathscr{y}^{(1)}$s, namely $\sqrt{[3/I(I+1)]}$, gives

$$I_\pm=\sum_M \sqrt{[(I+M)(I-M+1)]}\;I_\pm{}^{rs} \qquad (43)$$

where $I_\pm{}^{rs}$ is the fictitious spin-$\frac{1}{2}$ operator related to the $\mathscr{y}$s by

$$\mathscr{y}_{1/2}{}^{(1)\pm1}(M)=\mp i\sqrt{2}I_\pm{}^{rs}=\mp i\sqrt{2}(I_x{}^{rs}\pm iI_y{}^{rs}) \qquad (44)$$

with rs denoting the M, $M-1$ levels.

A hamiltonian containing spin operators all have their coupling magnitudes changed to effective constants when operating in multiplet spin space [3]. The form of these modifications depend on the hamiltonian and approximations of how the levels are uncoupled. Since descriptions of single quantum selective excitations are the same using fictitious or multiplet spin, the factors for the effective constants are the same.

5.8. *Multiplet spin density operator*

The use of the multiplet spins to decompose the total spin operators $\mathscr{I}^{(k)q}(\mathbf{I})$ is overcomplete and does not form an orthogonal basis between different multiplet spins. The only reason for constructing a multiplet spin and decomposing the total spin space must lie in some weak coupling between the multiplet spin and the total spin. In particular in selective excitation, irradiation near a well-separated line causes transition between only one set of levels. The multiplet spin thus defined then has spin properties and an orthonormal basis. Since all other levels are assumed to be unaffected, the multiplet spin density operator can be obtained,

$$\sigma_{I_M}(M)=\frac{1}{2I_M+1}\left[E_{I_M}+\sum_{p=1}^{2I_M}\sum_{q=-p}^{p}\phi_q{}^p(I_M M)\,\mathscr{I}_{I_M}{}^{(p)q}(M)\right]. \tag{45}$$

This obeys the quantum Liouville equation,

$$i\hbar\frac{\partial\sigma_{I_M}(M)}{\partial t}=[\mathscr{H},\,\sigma_{I_M}(M)]_-, \tag{46}$$

where $\mathscr{H}$ is the full spin hamiltonian.

6. Discussion of multipoles and multiplet spin

Each $\mathscr{I}^{(k)q}$ describes a multipole contribution to the qth quantum coherence of spin I. Since the multipole operator basis for a multiplet spin, namely $\mathscr{I}_{I_M}{}^{(k)q}(M)$ is mathematically equivalent to the $\mathscr{I}^{(k)q}$ for spin I_M, we first discuss the physical content of nuclear multipoles.

Consider an equilibrium population of a spin $I=3/2$ in a static magnetic field. A non-selective $\pi/2$ pulse transfers all the population into the xy plane and excites $\mathscr{I}^{(1)\pm1}(\mathbf{I})$. Internal interactions and subsequent pulses mix this coherence with other multipoles. Figure 3 *a* shows the contribution to the single quantum spectrum which arises from each multipole for $I=3/2$. Figures 3 (*b*) and 3 (*c*) show the double and triple quantum character. Of these operators, the usual N.M.R. experiment detects only $\mathscr{I}^{(1)\pm1}(\mathbf{I})$. In multiquantum N.M.R. after specific coherences are excited they are transferred to the $\mathscr{I}^{(1)\pm1}$ modes for detection. The final signal therefore depends on the past history of multipole character. The character can be seen at a glance from the matrix representations of the $\mathscr{I}^{(k)q}$s in the MM' basis given in table 1. Comparison of figures 3 with the corresponding matrix in table 1 shows single double triple etc. processes lie 1, 2, 3, etc. off the diagonal and the sign and magnitude of the contribution to the multiquantum processes is also evident from the matrix form.

The use of multipoles for describing spin systems can be compared to the use of orbitals to describe the electronic structure of atoms. The *spdf* . . . orbitals arise from a multipole expansion of the charge distribution about an atom. Each orbital has different multipole character which corresponds to orbital angular momentum. For a single nuclear spin, the formal multipole construction is the same. On one hand, however, an electrostatic potential, and on the other a hyperfine nuclear hamiltonian are responsible for the interactions. The hamiltonian mixes multipoles so that the state is a linear

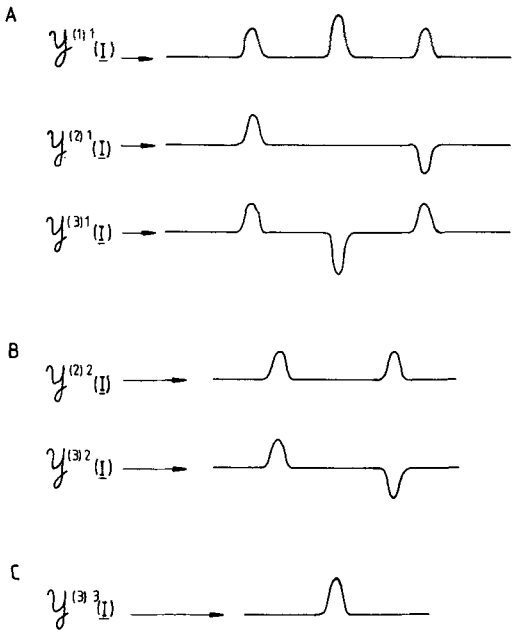

Figure 3. Multiquantum coherences decomposed into multipole character for (*a*) single quantum coherence, (*b*) double quantum coherences for $I=3/2$, and (*c*) triple quantum coherences.

combination of multipole operators. Each multipole has different properties just as the atomic orbitals differ in their character.

For $I=3/2$, ($k\leqslant 3$), the double quantum coherence can have both quadrupole (d-orbital) and octupole (f-orbital) character. The $I=3/2$ triple quantum coherence $\mathscr{y}^{(3)\pm 3}$ has only octupole character. In contrast $I=1$ has a double quantum coherence with only quadrupole character.

These ideas are straightforwardly generalized to multispin systems. Then it is necessary to take linear combinations of single-spin multipole operators and require the set to be orthogonal and rotationally invariant [9].

Turning now to selective excitation, it is shown how to extract the multiplet density operator from the full spin density operator without doing C–G algebra. Once this is done, the problem is reduced to a usual spin calculation, equation (46). Use is made of the representations of $\mathscr{y}^{(k)q}$s in table 1.

If a selective pulse is applied to the $I=1$, $M=1\leftrightarrow 0$ or $M=0\leftrightarrow -1$ levels, the equilibrium density operator can be written as

$$\sigma_1(t=0)=\tfrac{1}{3}\left[E_1+i\phi_0{}^1\sqrt{(\tfrac{3}{2})}\begin{pmatrix}1 & & \\ & 0 & \\ & & -1\end{pmatrix}\right]$$

$$=\tfrac{1}{3}[E_1+i\phi_0{}^1\,2\sqrt{6}(\sigma_{1/2}(1)+\sigma_{1/2}(0))]. \tag{47}$$

The two multiplet spin 1/2 density operators are

$$\sigma_{1/2}(1)=\tfrac{1}{2}E_{1/2}(1)+\tfrac{1}{2}\mathscr{y}_{1/2}{}^{(1)0}(1) \tag{48}$$

and

$$\sigma_{1/2}(0)=\tfrac{1}{2}E_{1/2}(0)-\tfrac{1}{2}\mathscr{Y}_{1/2}{}^{(1)0}(0), \tag{49}$$

where

$$E_{1/2}(1)=\begin{pmatrix}1 & & \\ & 1 & \\ & & 0\end{pmatrix}, \qquad E_{1/2}(0)=\begin{pmatrix}0 & & \\ & 1 & \\ & & 1\end{pmatrix}$$

$$\mathscr{Y}_{1/2}{}^{(1)0}(1)=i\begin{pmatrix}1 & & \\ & -1 & \\ & & 0\end{pmatrix}, \quad \mathscr{Y}_{1/2}{}^{(1)0}(1)=i\begin{pmatrix}0 & & \\ & 1 & \\ & & -1\end{pmatrix}. \tag{50}$$

A *selective* single quantum pulse is assumed to affect only one multiplet spin density operator, $\sigma_{1/2}(1)$ or $\sigma_{1/2}(0)$.

A double quantum excitation does not require further decomposition for spin I all three states being retained.

In practice it is not necessary to decompose the full $(2I+1)$ levels into various groups of multiplet spins. Rather it is only necessary to extract the $(2I_M+1)^2$ multiplet spin operators of interest; selectively excite them; and then re-embed them back into $(2I+1)^2$ space. Consider a spin $I=3/2$ and a double quantum process between $M=1/2$ and $-3/2$. The following construction can be used starting with the equilibrium $I=3/2$ density matrix (all matrices are diagonal and the identity operator for $I=3/2$, $E_{3/2}$, is moved to the right hand side),

$$\begin{aligned}&[\sigma_{3/2}(t=0)-\tfrac{1}{4}E_{3/2}]\\ &\quad=\phi_0{}^1\frac{i}{\sqrt{5}}\begin{pmatrix}3 & & & \\ & 1 & & \\ & & -1 & \\ & & & -3\end{pmatrix}\\ &\quad=\phi_0{}^1\frac{i}{\sqrt{5}}\begin{pmatrix}3 & & & \\ & -1 & & \\ & & -1 & \\ & & & -1\end{pmatrix}+\phi_0{}^1\frac{i}{\sqrt{5}}2\begin{pmatrix}0 & & & \\ & 1 & & \\ & & 0 & \\ & & & -1\end{pmatrix}\end{aligned} \tag{51}$$

The second term can be identified as $\phi_0{}^1\sqrt{(\frac{9}{15})}\mathscr{Y}_1{}^{(1)0}(1/2)$ (see table 1) which can be selectively changed by an appropriate selective pulse. In doing the separation, the population of the $(2I_M+1)$ levels of interest in the original matrix are first equalized so it appears as the identity for the I_M space. The portion left over (in this case $\mathscr{Y}_1{}^{(1)0}(1/2)$) characterizes the initial *multiplet* spin polarization.

As another example, to show that more complicated examples can be easily handled, consider a multiplet spin of 3/2 defined from levels $M=5/2$ to $-1/2$ of a spin of $I=7/2$. The equilibrium density operator for $I=7/2$ is

$$\sigma_{7/2}=\tfrac{1}{8}(E_{7/2}+\phi_0{}^1\ \mathscr{Y}^{(1)0}(\mathbf{I})) \tag{52}$$

with initial polarization of $\phi_0{}^1$. From (38) this is

$$(\sigma_{7/2}-\tfrac{1}{8}E_{7/2})=\tfrac{1}{8}\phi_0{}^1\frac{i}{\sqrt{(21)}}\begin{pmatrix}7\\5\\3\\1\\-1\\-3\\-5\\-7\end{pmatrix}, \tag{53}$$

where, for simplicity, we have written the diagonal matrix as a vector. It means, in fact, an 8×8 matrix in the $|IM\rangle\langle IM'|$ basis, but all the non-diagonal elements are zero. The trace of the $5/2->-1/2$ levels is $5+3+1-1=8$ so we leave $8/4=2$ as the equal contribution to each of the 4 multiplet states of interest. Subtracting the traceless part gives

$$(\sigma_{7/2}-\tfrac{1}{8}E_{7/2})=\tfrac{1}{8}\phi_0{}^1\frac{i}{\sqrt{21}}\left[\begin{pmatrix}7\\2\\2\\2\\2\\-3\\-5\\-7\end{pmatrix}+\begin{pmatrix}0\\3\\1\\-1\\-3\\0\\0\\0\end{pmatrix}\right]$$

$$=\tfrac{1}{8}\phi_0{}^1\frac{i}{\sqrt{21}}\begin{pmatrix}7\\2\\2\\2\\2\\-3\\-5\\-7\end{pmatrix}+[\sigma_{3/2}(\tfrac{5}{2})-\tfrac{1}{4}E_{3/2}(\tfrac{5}{2})], \tag{54}$$

where

$$\sigma_{3/2}(\tfrac{5}{2})=\tfrac{1}{4}[E_{3/2}(\tfrac{5}{2})+\phi_0{}^1(\tfrac{5}{2})\mathscr{Y}_{3/2}{}^{(1)0}(\tfrac{5}{2})]$$

$$=\tfrac{1}{4}\left[\begin{pmatrix}0\\1\\1\\1\\1\\0\\0\\0\end{pmatrix}+\phi_0{}^1\frac{i}{\sqrt{5}}\begin{pmatrix}0\\3\\1\\-1\\-3\\0\\0\\0\end{pmatrix}\right] \tag{55}$$

and $\phi_0{}^1(\frac{5}{2})=(\sqrt{5}/2\sqrt{(21)})\phi_0{}^1$. This shows that the multiplet spin $I_{5/2}=\frac{3}{2}$ gives the operator $\mathscr{Y}_{3/2}{}^{(1)0}(\frac{5}{2})$ (cf table 1, $I=3/2$).

For any spin I it is possible to take the full density operator either at equilibrium or with non-zero coherences and separate out the multiplet spin density

operator. After a selective interaction changes the multiplet spin density operator according to (46) the result can be put back into the full density operator for spin I. Such an approach reduces the treatment of selective multiquantum N.M.R. to non-selective multiquantum N.M.R. but on a spin I_M smaller than the total I.

7. Summary and discussion

In this paper we have discussed several spin constructions for a single spin :

(i) The total spin I with $(2I+1)$ levels and its multipole basis ;

(ii) the composite spin $I=1/2$ from which any I can be constructed ;

(iii) the fictitious spin-1/2 formalism which consists of a Pauli spin construction for all pairs of levels ;

(iv) the multiplet spin I_M composed of all nearest $(2I+1)$ multiplets which arise in the $(2I+1)$ manifold.

Which basis one uses depends to a large extent on the problem under study. The multipole basis $\mathscr{T}^{(k)q}$ being irreducible under SO(3), allows the powerful techniques of Racah algebra to be used. This means calculations need be done for spin I only once without having to do a separate calculation for each I. The approach is also easily adapted to numerical work when I becomes too large for analytic solution. Also a multispin operator basis [9] can be generated from $\mathscr{T}^{(k)q}$, again being irreducible under SO(3). Interpretation of the average multipoles $\phi_q^k = \langle \mathscr{T}_q^k \rangle$ has clear physical significance, namely describing the multipole character k and multiquantum coherence q. The multipole operator can be compared to the usual multipole expansion of a charge distribution. The construction and use of *spdf* . . . atomic orbitals is likewise based on a multipole series. Similar advantages are found in N.M.R. when multipole operators are used for expanding the nuclear distribution (see also [11–12]).

In contrast the basis I_ρ^{rs}, not being irreducible under SO(3) requires calculations based on Lie algebra. This makes numerical work difficult and, although general relations exist [5], it has so far been necessary to treat each spin magnitude separately. The polarization $\langle I_\rho^{rs} \rangle$ are physically less revealing for some aspects of multiquantum N.M.R. in part because $r-s$ does not correspond to a multiphoton process unless $p=x$ or y and pure pulses do not correspond to rotations unless $|\Delta M|=1$. Further working with an over complete and non-orthogonal basis has mathematical disadvantages.

The multiplet spin multipole basis like the fictitious spin-1/2 formalism is overcomplete and non-orthogonal when all the multiplet spins are used. The multiplet spin, however, has advantages when treating selective excitation of specific lines since only one multiplet spin is required, and its operator basis is complete and orthonormal. When single quantum processes are considered the multiplet spin and fictitious spin-1/2 treatments are the same. Multiquantum excitation in contrast, as caused by vector rf fields, results from a series of jumps between nearest levels and does not occur as a single $\Delta M=q$ transition. The intermediate levels are therefore important and the multiplet spin formulation permits them to be included.

Not treated in this work is the actual evolution of the multiplet spin density operator which is presented for single spins elsewhere [3].

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References

[1] See, e.g., Warren, W. S., and Pines, A., 1981, *J. chem. Phys.*, **74,** 2808 and references therein.
[2] Sanctuary, B. C., Halstead, T. K., and Osment, P., 1983, *Molec. Phys.* (in the press) (Paper IV).
[3] Sanctuary, B. C., 1983, *Molec. Phys.* (in the press) (Paper V).
[4] Vega, S., and Pines, A., 1977, *J. chem. Phys.*, **66,** 5624.
[5] Vega, S., 1978, *J. chem. Phys.*, **68,** 5518.
[6] Wokaun, A., and Ernst, R. R., 1977, *J. chem. Phys.*, **67,** 1752.
[7] Fano, U., 1957, *Rev. mod. Phys.*, **29,** 74.
[8] Edmonds, A. R., 1960, *Angular Momentum in Quantum Mechanics* (Princeton University).
[9] Sanctuary, B. C., 1976, *J. chem. Phys.*, **64,** 4352 (Paper I).
[10] Abragam, A., 1961, *The Principles of Nuclear Magnetism* (Clarendon Press), p. 36.
[11] Spiess, H. W., 1980, *J. chem. Phys.*, **72,** 6755.
[12] Fedders, P. A., and Lu, E. Y. C., 1973, *Phys. Rev.* B, **8,** 5156. Fedders, P. A., 1975, *Phys. Rev.*, **11,** 995; 1976, *Ibid.*, **13,** 2768.
[13] Bain, A., and Lynden-Bell, R. M., 1975, *Molec. Phys.*, **30,** 325. Bain, A., and Martin, J. S., 1978, *J. magn. Reson.*, **29,** 125, *Ibid.*, 137 ; 1980, *Ibid.*, **37,** 209.
[14] Pyper, N. C., 1971, *Molec. Phys.*, **21,** 1 ; 1971, *Ibid.*, **22,** 433; 1971, *Ibid.*, **22,**443.
[15] Lynden-Bell, R. M., 1971, *Molec. Phys.*, **22,** 837.
[16] Karl Blum, 1981, *Density Theory and Applications* (Plenum).
[17] Banwell, C. N., and Primas, H., 1963, *Molec. Phys.*, **6,** 225.
[18] Spiess, W., 1978, *NMR Basic Principles and Progress*, Vol. 15, edited by P. Diehl, E. Fluck and R. Kosfeld (Springer-Verlag).
[19] Chen, F. M., and Snider, R. F., 1969, *J. chem. Phys.*, **50,** 4082.
[20] Coope, J. A. R., Snider, R. F., and McCourt, F. R., 1965, *J. chem. Phys.*, **45,** 2264. Coope, J. A. R., and Snider, R. F., 1970, *J. math. Phys.*, **11,** 1103. Coope, J. A. R., 1970, *J. math. Phys.*, **11,** 1591.
[21] Boerner, H., 1963, *Representation of Groups* (North-Holland).
[22] Gibson, W. M., and Pollard, B. R., 1976, *Symmetry Principles in Elementary Particle Physics* (Cambridge University Press).
[23] Vega, S., and Naor, Y., 1981, *J. chem. Phys.*, **75,** 75.
[24] Mehring, M., Wolff, E. K., and Stoll, M. E., 1980, *J. magn. Reson.*, **37,** 475.
[25] Sanctuary, B. C., and Selwyn, L., 1978, *J. chem. Phys.*, **69,** 2157 ; 1981, *Ibid.*, **74,** 906.
[26] Jeener, J., and Broekaert, P., 1967, *Phys. Rev.*, **157,** 232.