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Operator Space Quantum Numbers for Spin Systems

B. C. SANCTUARY, NELSON LEE, F. COMMODARI, G. CAMPOLIETI, MANGALA S. KRISHNAN,* AND MIMI LAM†

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Canada H3A 2K6

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In direct analogy to ordinary state space describing N spins, $|IM\alpha\rangle$, there exist quantum operator states, $|kq\bar{\alpha}\rangle\rangle$. These operators form a complete basis set for states which are coherent and incoherent mixtures described by a density matrix. The quantum numbers labeling the operators are the multipole magnitude, k, the multiquantum coherence, q, and all other quantum numbers, $\bar{\alpha}$, needed to completely specify the states.

Magnetic resonance phenomena involving groups of coupled spins have been extensively studied over the last three decades. Pioneering research into ESR/EPR has been done by McDowell (*1–3*), and extensive review articles exist (*4, 5*). ESR techniques overlap with NMR in ENDOR (*6*) and dynamic nuclear polarization (*7–9*), and NMR often involves groups of interacting nuclear spins.

One of the most useful innovations to magnetic resonance has been the development of the fast Fourier transform and the use of pulse sequences. To study the response of spin systems to pulses, particularly because of the subsequent development of multiquantum coherences, a density matrix (*10*) treatment is essential. This is because the time dependence of a state $|IM\alpha\rangle$ cannot describe coherences between states in which the multiquantum coherences depend on the differences between M and M'. Nor can the pure state $|IM\alpha\rangle$ describe the incoherent mixture between states having the same M values which give rise to polarizations and alignments (*11*). In contrast, the quantum mechanical density operator, ρ, naturally accounts for these effects and describes the time evolution of the state of a system.

In this paper it is emphasized that the construction of the operator states can be achieved by using the same physical and mathematical considerations which are commonly applied to the states $|IM\alpha\rangle$. A set of labels for the operator states (i.e., states in Liouville space), $|kq\bar{\alpha}\rangle\rangle$, may be considered (*12*) to be quantum numbers which follow naturally from the rotational properties of angular momentum operators. In complete analogy to state space, spin operators can be coupled and recoupled

* Present address: Department of Chemistry, UBC, 2036 Main Mall, Vancouver, Canada V6T 1Y6.

† McGill, Department of Chemistry Visting Summer Scholar 1988 and NSERC Undergraduate Award Holder.

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TABLE 1

Parallel Construction between the Qunatum Mechanics of Angular Momentum for States and for Operators

States	Operators
Schrodinger equation	Quantum Liouville equation
$i\hbar \frac{\partial \psi}{\partial t} = \mathscr{H}\psi$	$i\hbar \frac{\partial \rho}{\partial t} = [\mathscr{H}, \rho]_- = \mathcal{L}\rho$
Spin states	Operator states
$\vert IM\alpha\rangle$	$\vert kq\bar{\alpha}\rangle\rangle$
Spin operator	Spin superoperator
$\mathbf{I}$	$\mathscr{I} = [\mathbf{I},]_-$
Effects of operators	Effects of commutators
$I^2 \vert IM\alpha\rangle = I(I+1) \vert IM\alpha\rangle$	$\mathscr{I}^2 \vert kq\bar{\alpha}\rangle\rangle = [\mathbf{I}\cdot[\mathbf{I}, \vert kq\bar{\alpha}\rangle\rangle]_-]_- = k(k+1) \vert kq\bar{\alpha}\rangle\rangle$
$I_z \vert IM\alpha\rangle = M \vert IM\alpha\rangle$	$\mathscr{I}_z \vert kq\bar{\alpha}\rangle\rangle = [I_z, \vert kq\bar{\alpha}\rangle\rangle]_- = q \vert kq\bar{\alpha}\rangle\rangle$
$I_\pm \vert IM\alpha\rangle = [I(I+1) - M(M \pm 1)]^{1/2} \vert IM \pm 1\alpha\rangle$	$\mathscr{I}_\pm \vert kq\bar{\alpha}\rangle\rangle = [k(k+1) - q(q \pm 1)]^{1/2} \vert kq \pm 1\alpha\rangle\rangle$
Wigner Eckart theorem	
$\langle IM\alpha \vert A^{lm} \vert IM'\alpha'\rangle = (-1)^{I-M} \times \begin{bmatrix} I & l & I \\ -M & m & M' \end{bmatrix} \langle I\alpha \Vert A^l \Vert I\alpha'\rangle$	$\langle\langle kq\bar{\alpha} \vert A^{lm} \vert k'q'\bar{\alpha}'\rangle\rangle = (-1)^{k-q} \times \begin{bmatrix} k & l & k' \\ -q & m & q' \end{bmatrix} \langle\langle k\bar{\alpha} \Vert A^l \Vert k'\bar{\alpha}'\rangle\rangle$
Principle of superposition	
$\psi = \sum_{IM\alpha} a_{IM\alpha} \vert IM\alpha\rangle$	$\rho = \sum_{kq\bar{\alpha}} \phi_q^k(\bar{\alpha}) \vert kq\bar{\alpha}\rangle\rangle$

in a variety of ways as the physical reality of strongly and weakly coupled spins dictates.

A variety of operator bases have been proposed for the density operator, many of these being described in the recent monograph by Ernst *et al.* (*13*). Use of one basis over another often depends on the problem to be treated. In the present paper, a parallel structure of quantum numbers from state to operator space will be described and a few examples will be provided.

STATE AND OPERATOR QUANTUM NUMBERS FOR SPINS

Table 1 shows the parallel construction between the quantum mechanics of angular momentum for states and for operators. Numerous books on angular momentum theory (*14–18*) derive these well-known equations for states. The existence of spin follows from the early observations by Stern and Gerlach (*19*) of silver atoms in an inhomogeneous magnetic field which subsequently led to the postulation of electron spin. The angular momentum vector operator **I** obeys the commutation relations,

$$\mathbf{I} \times \mathbf{I} = i\hbar\mathbf{I}. \qquad [1]$$

Nuclear spin and rotational and other angular momenta, of both integer and half-integer values, are known. In the case of magnetic resonance phenomena, the dominant interaction of angular momentum I is with an external magnetic field $\mathbf{B}(t)$. This interaction is described by the Zeeman Hamiltonian,

$$\mathscr{H}(t) = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}(t). \qquad [2]$$

Consider the simple case that $\mathbf{B}(t)$ is constant in time with value $\mathbf{B}_0$. In this case, the formal solution to the quantum Liouville equation (Table 1) is (*14, 18*)

$$\rho(t) = \exp(i\gamma \mathbf{B}_0 \cdot \mathbf{I}t)\rho(0)\exp(-i\gamma \mathbf{B}_0 \cdot \mathbf{I}t) \qquad [3]$$

$$\equiv \exp\{i\gamma t \mathbf{B}_0 \cdot \mathscr{I}\}\rho(0). \qquad [4]$$

The unitary operator

$$\mathscr{U} = \exp(-i\gamma t \mathbf{B}_0 \cdot \mathbf{I}) \qquad [5]$$

and superoperator

$$\mathscr{U}_{\mathcal{L}} = \exp(-i\gamma t \mathbf{B}_0 \cdot \mathscr{I}) \qquad [6]$$

have a familiar form. For example, a space translation operator is

$$\exp[-i\mathbf{r} \cdot \mathbf{p}/\hbar], \qquad [7]$$

where the conjugate variable to the momentum operator, $\mathbf{p}$, is the position operator, $\mathbf{r}$. Another example is time translation,

$$\exp[-it\mathscr{H}/\hbar], \qquad [8]$$

where the conjugate variable to the energy Hamiltonian is time, t. The form of interest here is a rotation generator,

$$\exp[-i\theta \cdot \mathbf{J}/\hbar], \qquad [9]$$

where the conjugate variable to the angular momentum operator $\mathbf{J}$ is the set of angles θ. The rotational unitary operator [9] has the same form as that of [5]. One is therefore led to finding the solutions to the Zeeman interaction in terms of the symmetry of the rotation group.

One way of viewing this is to study the rigid rotor problem quantum mechanically. The solution is found to give rise to quantum numbers J and M with the energy depending only on J. The Zeeman interaction lifts the M degeneracy and gives rise to the nomenclature where the M's label the magnetic quantum numbers. The point here is that the quantum numbers labeled by J and M are not chosen; they arise naturally. One has no choice over quantum numbers since they arise from the form of the Hamiltonian alone.

In the case of a spin I, the rotational property of the Zeeman interaction means that the only states that can be obtained are simply rotated one to the other,

$$\mathscr{U}(\omega)|IM\rangle = \sum_{M'=-I}^{I} \langle IM'|\mathscr{U}|IM\rangle|IM'\rangle = \sum_{M'=-I}^{I} \mathscr{D}^{(I)}_{M'M}(\omega)|IM'\rangle, \qquad [10]$$

where $\mathscr{D}^{(I)}_{M'M}(\omega)$ are Wigner rotation matrices (*14–18*) and ω is a shorthand notation for the Euler angles.

It is possible to construct operator states in exact analogy to the state quantum numbers I and M or J and M, with parallel properties, *only if the operators are chosen to be spherical tensor operators irreducible under the rotation group.* Denoting these by $|kq\rangle\rangle$, it follows (*14–18*) that under the Zeeman Hamiltonian,

$$\mathcal{U}_{\mathcal{L}}(\omega)|kq\rangle\rangle \equiv \mathcal{U}(\omega)|kq\rangle\rangle\mathcal{U}^{-1}(\omega) \quad [11]$$

$$= \sum_{q'} \mathcal{D}^{(k)}_{q'q}(\omega)|kq'\rangle\rangle. \quad [12]$$

Other notations for writing the spherical tensor operators used by the authors are

$$|kq\rangle\rangle = \mathcal{Y}^{(k)q}(\mathbf{I}) \quad [13]$$

$$\propto T^{kq}(\mathbf{I}), \quad [14]$$

where these may differ by a phase and normalization constant. Other approaches using spherical tensor operators have been reviewed (*20*). All properties of states $|IM\alpha\rangle$ carry naturally over to operators $|kq\bar{\alpha}\rangle\rangle$ such as the Wigner Eckart theorem (Table 1) and Clebsch–Gordan coupling.

Therefore, when treating magnetic resonance problems where a density matrix description is required, one may use a spherical tensor operator basis with quantum numbers k and q. It makes sense to choose the basis so that it transforms as simply as possible under rotations. The choice of an operator basis as being irreducible under rotations is a natural extension of state vectors $|IM\rangle$ (which for integer spin may be represented by spherical harmonics, $Y_{IM}(\theta,\phi)$) to $|kq\rangle\rangle$, leading to the notation $\mathcal{Y}^{(k)q}(\mathbf{I})$ for the spherical tensor operator states. Thus, the spin angular momentum states are labeled by $|IM\rangle$, where the labels IM denote the irreducible representation in the state basis, reflecting the symmetry of the Hamiltonian. In the same way, the spherical tensor operators, $\mathcal{Y}^{(k)q}(\mathbf{I})$, form an irreducible operator (rather than state) basis with labels k and q.

For multispin systems $|IM\rangle$ is generalized to $|IM\alpha\rangle$ and $|kq\rangle\rangle$ to $|kq\bar{\alpha}\rangle\rangle$ (also denoted by $T^{kq}(\bar{\alpha})$).

DISCUSSION OF OPERATOR SPACE CONSTRUCTION

For any nuclear spin Hamiltonian, the operators $|kq\rangle\rangle$ form a complete set of basis operators for a single spin with the range of values depending on the spin magnitude I,

$$0 \leqslant k \leqslant 2I \quad [15]$$

and

$$-k \leqslant q \leqslant +k. \quad [16]$$

It is easy to show (*12, 21*) that k is the tensor rank of the operator and in fact describes the order of the multipoles associated with a particular spin polarization. Similarly q is the spherical component of the tensor but also labels the difference in M values in matrix elements of operators of the type T^{kq}. Hence $q = \Delta M$ describes the multi-quantum coherences. As other interactions become important, the k and q

labels are no longer good quantum numbers, and the eigenoperators will be a superposition of $|kq\rangle\rangle$'s (*22*).

In describing groups of coupled spins, the relative strength of coupling determines how the operators are constructed. Consider N different spins, with no interaction other than the Zeeman Hamiltonian. States may be chosen as the product

$$|I_1M_1\rangle|I_2M_2\rangle\cdots|I_NM_N\rangle = |I_1M_1I_2M_2\cdots I_NM_N\rangle. \qquad [17]$$

Likewise, and in analogy with [17], product operators are found

$$\mathcal{Y}^{(k_1)q_1}(I_1)\mathcal{Y}^{(k_2)q_2}(I_2)\cdots\mathcal{Y}^{(k_N)q_N}(I_N) \qquad [18]$$

for describing groups of weakly coupled spins. For spins of $I_i = \frac{1}{2}$, k_i has values of 0 and 1 and $q_i = 0, \pm 1$.

Product operator formalisms have found utility in describing two-dimensional spectra obtained by, for example, the COSY sequence (*13, 23–25*). Whereas some people (*25*) use a product operator formalism of the type $|k_1k_2\cdots k_Nq_N\rangle\rangle$, others (*13, 23, 24*) prefer the Cartesian product operators,

$$I_j^1I_k^2\cdots I_l^N, \qquad [19]$$

where $j, k, \ldots, l$ are any of the Cartesian labels x, y, and z.

Spin couplings do not act with equal strength. For N strongly coupled spins, the Hilbert state space is denoted by

$$|IM\alpha\rangle \qquad [20]$$

with

$$\mathbf{I} = \sum_{i=1}^{N} \mathbf{I}_i. \qquad [21]$$

The Hilbert operator space is

$$|kq\bar{\alpha}\rangle\rangle. \qquad [22]$$

In the preceding, α or $\bar{\alpha}$ account for all intermediate coupling quantum numbers.

For example, two coupled spins of magnitude I_1 and I_2 give rise to the coupled states

$$|IM(I_1I_2)\rangle \qquad [23]$$

and the corresponding operator states are

$$|kq(k_1k_2)\rangle\rangle. \qquad [24]$$

The range of k is defined by the triangular inequality

$$|k_1 - k_2| \leqslant k \leqslant k_1 + k_2, \qquad [25]$$

and as always $-k \leqslant q \leqslant k$. The values of k_1 and k_2 are bounded by 0 and, respectively,

TABLE 2

Two Coupled Spins of $I = \frac{1}{2}$

Basis $\|k\ k_1\ k_2\rangle\rangle$	No. of components	Notation (A)	Notation (B)
		Identity	
$\|0\,0\,0\,0\rangle\rangle$	1	E	(e1e2)
		Scalar dot product	
$\|0\,0\,1\,1\rangle\rangle$	1	$\mathbf{I}_1 \cdot \mathbf{I}_2$	$(\mathrm{d1d2})^0$
		Components for spin 1	
$\|1\,q\,1\,0\rangle\rangle$	3	$\mathbf{I}_1$	$(\mathrm{d1})^{1q}$
		Components for spin 2	
$\|1\,q\,0\,1\rangle\rangle$	3	$\mathbf{I}_2$	$(\mathrm{d2})^{1q}$
		Vector cross product	
$\|1\,q\,1\,1\rangle\rangle$	3	$\mathbf{I}_1 \times \mathbf{I}_2$	$(\mathrm{d1d2})^{1q}$
		Components of a second rank symmetric traceless tensor	
$\|2\,q\,1\,1\rangle\rangle$	5	$[\mathbf{I}_1\mathbf{I}_2]^2$	

Note. (A) Unnormalized representations of $|k\,q\,k_1\,k_2\rangle\rangle$ in terms of the vector couplings of $\mathbf{I}_1$ and $\mathbf{I}_2$. Superscripts denote the tensor rank. (B) d1, d2, dipole of spin 1 or 2. q represents the tensor component or multiquantum coherences, ΔM. e1, e2, identity states of spins 1 and 2.

$2I_1$ and $2I_2$. Table 2 gives the meaning of the labels for two coupled spins of $\frac{1}{2}$. Although magnetic resonance experiments detect only the spin vectors, the bilinear operators play important roles in polarization transfer and developments between pulses in multipulse sequences.

As the magnitude of the spins increases, so does the number of quantum numbers. Since a spin-$\frac{1}{2}$ and spin-1 are usually best treated as a product rather than a coupled pair, it is instructive to skip to the quantum numbers for two coupled spins of magnitude 1. There are 81 operators, as seen in Table 3. Although the meaning of these operators may appear vague, they are no more abstract than all the intermediate states of $|IM(11)\rangle$ and are considerably clearer than the operator $|IM(11)\rangle\langle I'M'(11)|$ in many cases.

Clearly, as the magnitude and number of spins increases, the number of quantum numbers rapidly proliferate. Fortunately, the techniques of angular momentum theory (*14–18*) can easily keep track of these without having to display them in detail or generate large tables of commutation relations.

TABLE 3

Two Coupled Spins of $I = 1$

Basis $\|k\,q\,k_1\,k_2\rangle\rangle$	No. of components	Notation (A)	Notation (B)
		Identity	
0 0 0 0	1	E	(e1e2)
		Scalars	
0 0 1 1	1	$\mathbf{I}_1 \cdot \mathbf{I}_2$	$[\mathrm{d1d2}]^0$
0 0 2 2	1	$[\mathbf{I}_1]^2 : [\mathbf{I}_2]^2$	$[\mathrm{Q1Q2}]^0$
		Vectors	
1 q 1 0	3	$\mathbf{I}_1$	$[\mathrm{d1}]^{1q}$
1 q 0 1	3	$\mathbf{I}_2$	$[\mathrm{d2}]^{1q}$
1 q 1 1	3	$\mathbf{I}_1 \times \mathbf{I}_2$	$[\mathrm{d1d2}]^{1q}$
1 q 2 1	3	$[\mathbf{I}_1]^2 \cdot \mathbf{I}_2$	$[\mathrm{Q1d2}]^{1q}$
1 q 1 2	3	$\mathbf{I}_1 \cdot [\mathbf{I}_2]^2$	$[\mathrm{d1Q2}]^{1q}$
1 q 2 2	3	$[[\mathbf{I}_1]^2[\mathbf{I}_2]^2]^1$	$[\mathrm{Q1Q2}]^{1q}$
		Second rank tensors	
2 q 2 0	5	$[\mathbf{I}_1]^2$	$[\mathrm{Q1}]^{2q}$
2 q 0 2	5	$[\mathbf{I}_2]^2$	$[\mathrm{Q2}]^{2q}$
2 q 1 1	5	$[\mathbf{I}_1\mathbf{I}_2]^2$	$[\mathrm{d1d2}]^{2q}$
2 q 2 1	5	$[\mathbf{I}_1]^2 \times \mathbf{I}_2$	$[\mathrm{Q1d2}]^{2q}$
2 q 1 2	5	$\mathbf{I}_1 \times [\mathbf{I}_2]^2$	$[\mathrm{d1Q2}]^{2q}$
2 q 2 2	5	$[[\mathbf{I}_1]^2[\mathbf{I}_2]^2]^2$	$[\mathrm{Q1Q2}]^{2q}$
		Third rank tensors	
3 q 1 2	7	$[\mathbf{I}_1[\mathbf{I}_2]^2]^3$	$[\mathrm{d1Q2}]^{3q}$
3 q 2 1	7	$[[\mathbf{I}_1]^2\mathbf{I}_2]^3$	$[\mathrm{Q1d2}]^{3q}$
3 q 2 2	7	$[[\mathbf{I}_1]^1[\mathbf{I}_2]^2]^3$	$[\mathrm{Q1Q2}]^{3q}$
		Fourth rank tensor	
4 q 2 2	9	$[[\mathbf{I}_1]^2[\mathbf{I}_2]^2]^4$	$[\mathrm{Q1Q2}]^{4q}$
	81		

Note. (A) Unnormalized representations of $|k\,q\,k_1\,k_2\rangle\rangle$ in terms of the vector couplings of $\mathbf{I}_1$ and $\mathbf{I}_2$. Superscripts denote the tensor rank. (B) d1, d2, dipole of spin 1 or 2. Q1, Q2, quadrupole of spin 1 or 2. q represents the tensor component or multiquantum coherences, ΔM. e1, e2, identity states of spins 1 and 2.

As a final example of a strongly coupled basis, we show in Table 4 three coupled spins of $\frac{1}{2}$. In this case, the 64 operators depend on the order in which the spins are coupled (i.e., the intermediate quantum label $\overline{\alpha}$ is dependent on the order of

TABLE 4

Three Coupled Spins of $I = \frac{1}{2}$

Basis $\vert k\,q\,k_1\,k_2\,k_3\,K\rangle\rangle$	No. of components	Notation (A)	Notation (B)
		Identity	
0 0 0 0 0 0	1	E	(e1e2)
		Scalars	
0 0 1 1 0 0	1	$\mathbf{I}_1 \cdot \mathbf{I}_2$	$[(d1d2)]^0$
0 0 1 0 1 1	1	$\mathbf{I}_1 \cdot \mathbf{I}_3$	$[(d1d3)]^0$
0 0 0 1 1 1	1	$\mathbf{I}_2 \cdot \mathbf{I}_3$	$[(d2d3)]^0$
0 0 1 1 1 1	1	$(\mathbf{I}_1 \times \mathbf{I}_2) \cdot \mathbf{I}_3$	$[(d1d2)_1 d3]^0$
		Vectors	
1 q 1 0 0 1	3	$\mathbf{I}_1$	$[d1]^{1q}$
1 q 0 1 0 1	3	$\mathbf{I}_2$	$[d2]^{1q}$
1 q 0 0 1 0	3	$\mathbf{I}_3$	$[d3]^{1q}$
1 q 1 1 0 1	3	$\mathbf{I}_1 \times \mathbf{I}_2$	$[(d1d2)]^{1q}$
1 q 1 0 1 1	3	$\mathbf{I}_1 \times \mathbf{I}_3$	$[d1d3)]^{1q}$
1 q 0 1 1 1	3	$\mathbf{I}_2 \times \mathbf{I}_3$	$[(d2d3)]^{1q}$
1 q 1 1 1 0	3	$(\mathbf{I}_1 \cdot \mathbf{I}_2) \times \mathbf{I}_3$	$[(d1d2)_0 d3]^{1q}$
1 q 1 1 1 1	3	$[\mathbf{I}_1 \times \mathbf{I}_2] \times \mathbf{I}_3$	$[(d1d2)_1 d3]^{1q}$
1 q 1 1 1 2	3	$[\mathbf{I}_1\mathbf{I}_2]^2 \cdot \mathbf{I}_3$	$[(d1d2)_2 d3]^{1q}$
		Second rank tensors	
2 q 1 1 0 2	5	$[\mathbf{I}_1\mathbf{I}_2]^2$	$[(d1d2)]^{2q}$
2 q 1 0 1 1	5	$[\mathbf{I}_1\mathbf{I}_3]^2$	$[(d1d3)]^{2q}$
2 q 0 1 1 1	5	$[\mathbf{I}_2\mathbf{I}_3]^2$	$[(d2d3)]^{2q}$
2 q 1 1 1 1	5	$[(\mathbf{I}_1 \times \mathbf{I}_2)\mathbf{I}_3]^2$	$[(d1d2)_1 d3]^{2q}$
2 q 1 1 1 2	5	$[\mathbf{I}_1\mathbf{I}_2]^2 \times \mathbf{I}_3$	$[(d1d2)_2 d3]^{2q}$
		Third rank tensor	
3 q 1 1 1 2	7 / 64	$[\mathbf{I}_1\mathbf{I}_2\mathbf{I}_3]^3$	$[(d1d2)]d3]^{3q}$

Note. (A) Unnormalized representations of $\vert k\,q\,k_1\,k_2\,k_3\,K\rangle\rangle$ in terms of the vector couplings of $\mathbf{I}_1$, $\mathbf{I}_2$, and $\mathbf{I}_3$. Superscripts denote the tensor rank. (B) d1, d2, dipole of spin 1, 2, or 3. q represents the tensor component or multiquantum coherences, ΔM. e1, e2, e3, identity states of spins 1, 2, and 3.

coupling). Consider first that spins 1 and 2 are coupled to give a resultant $\bar{k}$ with values

$$0 \leqslant \bar{k} \leqslant 2 \qquad [26]$$

and that this resultant is coupled to spins to give an operator state denoted by

$|kq\{(k_1k_2)\bar{k}, k_3\}\rangle\rangle$. However, if spins 1 and 3 are coupled first to give $\bar{k}'$, and subsequently coupled to spin 2, the resultant operator is denoted by $|kq\{(k_1k_3)\bar{k}', k_2\}\rangle\rangle$. The two operator states differ only by a unitary transformation and the relation between the two sets of states is given by a matrix of $6-j$ coefficients (*14*).

In magnetic resonance, it often occurs that a group of strongly coupled spins is weakly coupled to another. The notation found in the NMR literature (*26*) is, for example, A_2X, AMX, A_NX_M, AA′BB′, etc. When electron spin is present, it is always treated as weakly coupled to nuclear spins. The operators for these cases are given by

$$|kqk_1^{A}k_2^{A}\rangle\rangle|k^{X}q^{X}\rangle\rangle \quad [27]$$

for A_2X;

$$|kqk_1^{A}k_2^{A}k_3^{A}\bar{k}\rangle\rangle|k^{X}q^{X}\rangle\rangle \quad [28]$$

for A_3X;

$$|k^{A}qk_1^{A}k_2^{A}k_3^{A}k_4^{A}\bar{k}_1\bar{k}_2\rangle\rangle|k^{X}q^{X}k_1^{X}k_2^{X}\rangle\rangle \quad [29]$$

for A_4X_2; and

$$|k^{A}q^{A}\rangle\rangle|k^{M}q^{M}\rangle\rangle|k^{X}q^{X}\rangle\rangle \quad [30]$$

for AMX.

These examples show the procedures and underscore the parallel description for states.

CONCLUSION

In this paper, using the standard methods of angular momentum theory, an operator basis has been described that should be used if the symmetries and algebra which are used in state space are to be retained in the description of multiquantum processes in magnetic resonance phenomena. Although it is not usual to do so, it is beneficial to view the labels in operator space as quantum numbers with different, but complementary, meaning to the quantum numbers commonly used in state space.

Spin dynamics can be treated within any convenient basis and spherical tensors provide one. When relaxation is included in the treatments an additional simplicity arises in the spherical tensor basis. If the relaxation operator R is a scalar operator or depends only on $B_0\hat{z}$, then matrix elements in a spherical tensor basis are diagonal in k and q.

$$\langle\langle kq\bar{\alpha}|R|k'q'\bar{\alpha}'\rangle\rangle = \frac{1}{T_{kq}(\bar{\alpha}\bar{\alpha}')}\,\delta_{kk'}\delta_{qq'}. \quad [31]$$

For single spin systems in solids, this appears to be true (*27*).

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REFERENCES

1. P. H. FISCHER, S. W. CHARLES, AND C. A. MCDOWELL, *J. Chem. Phys.* **46**, 2162 (1967).
2. W. C. LIN, C. A. MCDOWELL, AND D. J. WARD, *J. Chem. Phys.* **49**, 2883 (1968).
3. C. A. MCDOWELL, H. NAKAJIMA, AND P. RAGHUNATHAN, *Can. J. Chem.* **48**, 805 (1970).
4. C. A. MCDOWELL, (ED.). "International Review of Science, Physical Chemistry," Series 2, Vol. 4, "Magnetic Resonance," Butterworths, London, 1975.
5. P. W. ATKINS, *Spec. Period. Rep.* **2**, 52 (1974).
6. G. FEHER, *Phys. Rev.* **103**, 834 (1956).
7. A. W. OVERHAUSER, *Phys. Rev.* **92**, 411 (1953).
8. I. SOLOMON AND N. BLOEMBERGEN, *J. Chem. Phys.* **25**, 261 (1956).
9. R. KAISER, *J. Chem. Phys.* **39**, 2435 (1963).
10. U. FANO, *Rev. Mod. Phys.* **29**, 74 (1957).
11. T. K. HALSTEAD, P. OSMENT, AND B. C. SANCTUARY, *J. Magn. Reson.* **60**, 382 (1984).
12. B. C. SANCTUARY, *J. Magn. Reson.* **61**, 116 (1985).
13. R. R. ERNST, G. BODENHAUSEN, AND A. WOKAUN, "Principles of Nuclear Magnetic Resonance in One and Two Dimensions," Clarendon, London/New York, 1987.
14. A. R. EDMONDS, "Angular Momentum in Quantum Mechanics," Princeton Univ. Press, Princeton, New Jersey, 1974.
15. U. FANO AND G. RACAH, "Irreducible Tensorial Sets," Academic Press, New York/London, 1959.
16. E. P. WIGNER, "Group Theory, and Its Applications to Quantum Mechanics of Atomic Spectra," Academic Press, New York/London, 1959.
17. M. E. ROSE, "Elementary Theory of Angular Momentum," Wiley, New York, 1957.
18. B. L. SILVER, "Irreducible Tensor Methods, An Introduction for Chemists," Academic Press, New York, 1976.
19. O. STERN AND W. GERLACH, *Z. Phys.* **8**, 110 (1922).
20. A. D. BAIN, *Prog. NMR Spectrosc.* **20**, 295 (1988).
21. B. C. SANCTUARY, *J. Chem. Phys.* **64**, 4352 (1976).
22. B. C. SANCTUARY AND M. S. KRISHNAN, *J. Magn. Reson.* **69**, 210 (1986).
23. O. W. SØRENSEN, G. W. EICH, M. H. LEVITT, G. BODENHAUSEN, AND R. R. ERNST, *Prog. NMR Spectrosc.* **16**, 163 (1983).
24. J.-PH. GRIVET, *J. Magn. Reson.* **62**, 269 (1985).
25. L. R. BROWN AND J. BREMER, *J. Magn. Reson.* **68**, 217 (1986).
26. E. D. BECKER, "High Resolution NMR: Theory and Chemical Applications," Academic Press, New York, 1980.
27. T. K. HALSTEAD, P. OSMENT, J. TEGENFELDT, I. LOWE, AND B. C. SANCTUARY, *J. Magn. Reson.* **67**, 267 (1986).