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Multipole N.M.R.
XI. Scalar spin coupling

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The multipole formulation of N.M.R. is applied to small spin systems interacting via scalar coupling. Two scalar coupled spins of 1/2 are treated in detail for bases that are irreducible under the rotation group, SO(3). Particular attention is focused on the role of the bilinear operators in providing a pathway for coupling. A complete analytical solution for the two spin-1/2 problem is given.

1. INTRODUCTION

In this paper the problem of spin coupling is studied partly to show how the multipole formulation of N.M.R. can be applied to the spin dynamics of several spins and partly to prepare the way for the treatment of spin decoupling [1] and multipulse sequences. The usual description of spin coupling focuses upon the operator $\mathbf{I}_1 \cdot \mathbf{I}_2$ stating that one spin interacts with a local magnetic field on spin 2 given by $J\mathbf{I}_2$ [2]. Since dipole operators are vectors, the mechanism of spin coupling is easily visualized. One of the major goals of N.M.R. spectroscopy is to suppress additional frequencies caused by unwanted scalar coupling in order to simplify the spectrum.

The mechanisms by which coupling and decoupling occurs, however, have not been fully analysed. One of the problems in a detailed analysis is that polarizations which are unobservable in the N.M.R. experiment, are responsible for coupling the spins together. In order to follow the coupling and decoupling mechanisms, it is necessary to follow the time evolution of all polarizations. Stated otherwise, the full density matrix needs to be calculated from all initial conditions.

In this paper the problem of spin coupling is reanalysed in terms of the multipole formulation and a physical picture is developed which involves observables other than spin vectors. The problem of two scalar coupled spins of 1/2 presented here brings out new features of particular relevance to pulsed N.M.R. In particular, the multiquantum coherences are evaluated to show how any state-preparing pulse will change the FID, or spectrum; from such considerations, some hints on how to decouple interacting spins may be inferred. In fact a rigorous formulation is obtained for the polarization which Levitt *et al.* [3] note gives illusions of decoupling. Although for two spins of 1/2, the dimensionality of the problem is low, it will be shown in a later publication [4] how to achieve additional factorization in Liouville space representations by the use of magnetic point group symmetry of spin systems to give the beneficial reduction in the dimensionality of the individual multiquantum domains.

This work runs parallel to the development of the superspin formulation of Bain [5] which also uses the Liouville approach [6, 7, 8]. In particular, scalar coupled spin systems have been discussed to give the effect of a resonant pulse on one of the spins [9, 10, 11]. These treatments use a spherical tensor operator basis which for AX systems is a product of the individual superspin bases. In this work, the basis used is the coupled one, denoted by $T^{kq}(k_1k_2)$ for two spins. The results of either formulation should be the same and the full density matrix can be calculated. An advantage of the $T^{kq}(k_1k_2)$ basis is that it ensures the bilinear operators are spherical tensors.

The treatment aims at being exact and, in the case of two scalar coupled spins of 1/2, this is possible. Often the coupling term $J\mathbf{I}_1 \cdot \mathbf{I}_2$ is truncated to $JI_{1z}I_{2z}$ [9, 11], especially when treating AX type problems. In the formulation presented here, truncation provides no simplification or convenience and the full term is retained. Hence we treat AB and AX systems simultaneously. For AX spin systems, for example, the limit $|\omega_D| \equiv 1/2|\omega_{01} - \omega_{02}| \gg J$ can later be invoked to give the effects of the truncated coupling term. The Larmor frequencies are $\omega_{0i} = \gamma_i B_0$.

One of the objects of this paper is to have a concise complete solution to the fully coupled 2 spin 1/2 problem. With this in mind, the zeroth and double quantum coherences as well as the single quantum coherence, from *any* initial state are given in a compact form. Section 2 describes the basis and hamiltonian with a physical interpretation of the basis being given. Section 3 derives the full set of equations which are exactly solved for zero, single and double quantum processes, while §4 gives a physical interpretation of the coupling process. Throughout the paper attention is entirely on the spin dynamics and relaxation is not included. (See [12, 13]).

2. Multipole basis and hamiltonians for 2 spins of 1/2

2.1. *Multipole basis*

Approaches to studying N.M.R. spectra often start with some initial state, say $|m_1m_2\rangle$ and calculate the transition probability

$$P_{m_1m_2 \to m_1'm_2'} = |C_{m_1'm_2'}(t)|^2, \tag{1}$$

where $C_{m_1'm_2'}$ are the probability amplitudes. One difficulty encountered in this approach is that the initial state is usually not pure but rather a mixture of many different states, suitably prepared by the past history of pulses and/or evolutions. When this occurs, it is necessary to use a density matrix, which for pure states, $P_{m_1m_2 \to m_1'm_2'}$ is an element. For a mixed state, the spin density operator is

$$\sigma(t) = \sum_{\substack{m_1m_2 \\ m_1'm_2'}} |m_1m_2\rangle \sigma_{m_1m_2}^{m_1'm_2'} \langle m_1'm_2'| \tag{2}$$

and the spin density matrix elements $\sigma_{m_1m_2}^{m_1'm_2'}$ give the transition probabilities at time t subject to an initial condition $\sigma(0)$. On the other hand, it is often difficult to visualize which states are initially produced in the $|m_1m_2\rangle$ basis in pulsed N.M.R.

It is possible, however to apply a unitary transformation to the operators $|m_1m_2\rangle\langle m_1'm_2'|$ and thereby reorganize the basis into a sum over various multipoles. The multipole operator basis [14] denoted by $T^{kq}(k_1k_2)$ spans the space of two spins. The parameter k denotes the tensor rank and q denotes the spherical component. The parameter k_i gives the tensor rank of the multipole operator for spin i; k_i values running from 0 to $2I_i$. The overall tensor rank k runs from 0 to $2(I_1 + I_2)$, and the spherical component q gives the order of the multiquantum process,

$$q = m_1 + m_2 - m_1' - m_2'. \quad (3)$$

For single spins, the multipole operators [14, 15] are $\mathscr{Y}^{(k_i)q_i}(\mathbf{I}_i)$ and are related to the two spin operators by

$$T^{kq}(k_1k_2) = [(2I_1 + 1)(2I_2 + 1)]^{-1/2} \sum_{q_1q_2} (-1)^{k_1-k_2+k} \sqrt{(2k+1)} \times (-1)^{k-q} \begin{pmatrix} k & k_1 & k_2 \\ -q & q_1 & q_2 \end{pmatrix} \mathscr{Y}^{(k_1)q_1}(\mathbf{I}_1)\mathscr{Y}^{(k_2)q_2}(\mathbf{I}_2). \quad (4)$$

These operators are spherical components of tensors, all of which are irreducible under the rotation group and first discussed in detail in 1976 [14]. This basis is valid for any spin magnitudes and not restricted to spins of 1/2. In the case of two spins of 1/2, a basis similar to $T^{kq}(k_1k_2)$ was given in table 2 of Bain [7] in 1978. Table 1 shows the relationship between the two notations and, apart from a phase difference, the two are the same. Bain has used this basis to treat (spin 1/2) *AB* problems [9] and the product basis, ($|1q_1\rangle|1q_2\rangle$ proportional to $\mathscr{Y}^{1q_1}(\mathbf{I}_1)\mathscr{Y}^{1q_2}(\mathbf{I}_2)$) is used to study (spin 1/2) *AX* problems [10, 11]. Pyper [16] also describes a multipole basis but he uses the notation $T^{kq}(I_1I_2)$ in which the meaning of I_1 and I_2 is confused with the spin magnitudes. In fact, he restricts his basis to integer spin only and I_1 and I_2 can vary. All these treatments make use of the spherical tensor properties to calculate matrix elements of the hamiltonian. It is common place to write the hamiltonian in terms of irreducible spherical tensors. In addition, multipole or superspin treatments also expand the spin space $|m_1m_2\rangle\langle m_1'm_2'|$ in irreducible spherical tensors. These are closely related to spherical harmonics (as far as rotation properties are concerned) and can be visualized as nuclear spin polarization orbitals in analogy to electronic orbitals [17]. For two spins of 1/2, the highest orbital character is $k = 2$ (d orbital or quadrupole character). Apart from mathematical advantages, multipoles also have useful physical properties.

Table 1. Relationship between the multipole basis $T^{kq}(k_1k_2)$ [14] and superspin basis [7]. q values range from $-k$ to $+k$.

Multipole basis	Superspin basis
$T^{00}(00)$	$\|0)\|0)$
$T^{00}(11)$	$\|0, 2)$
$T^{1q}(10) + T^{1q}(01)$	$\|1_q^s, 1)$
$T^{1q}(10) - T^{1q}(01)$	$\|1_q^a, 1)$
$T^{1q}(11)$	$\|1_q, 2)$
$T^{2q}(11)$	$\|2_q, 2)$

Table 2. Relation of multipole polarization to transition probabilities for a two spin-1/2 system.

$\langle | m'_1 m'_2 \rangle \langle m_1 m_2 | \rangle$

Zero quantum $q = 0$

$$\langle | \mp\tfrac{1}{2} \mp \tfrac{1}{2} \rangle \langle \mp\tfrac{1}{2} \mp \tfrac{1}{2} | \rangle = \frac{1}{2}\,\phi_0^0(00) + \frac{1}{\sqrt{12}}\,\phi_0^0(11) \mp \frac{i}{2}\,\phi_0^1(01) \mp \frac{i}{2}\,\phi_0^1(10) - \frac{1}{\sqrt{6}}\,\phi_0^2(11)$$

$$\langle | \mp\tfrac{1}{2} \pm \tfrac{1}{2} \rangle \langle \mp\tfrac{1}{2} \pm \tfrac{1}{2} | \rangle = \frac{1}{2}\,\phi_0^0(00) - \frac{1}{\sqrt{12}}\,\phi_0^0(11) \pm \frac{i}{2}\,\phi_0^1(01) \mp \frac{i}{2}\,\phi_0^1(10) + \frac{1}{\sqrt{6}}\,\phi_0^2(11)$$

$$\langle | \mp\tfrac{1}{2} \pm \tfrac{1}{2} \rangle \langle \pm\tfrac{1}{2} \mp \tfrac{1}{2} | \rangle = \frac{1}{\sqrt{3}}\,\phi_0^0(11) \pm \frac{1}{\sqrt{2}}\,\phi_0^1(11) + \frac{1}{\sqrt{6}}\,\phi_0^2(11)$$

Single quantum $q = \pm 1$

$$\langle | -\tfrac{1}{2} \mp \tfrac{1}{2} \rangle \langle -\tfrac{1}{2} \pm \tfrac{1}{2} | \rangle = \frac{\mp i}{\sqrt{2}}\,\phi_{\pm 1}^1(01) \mp \frac{1}{\sqrt{2}}\,\chi_{\pm 1}^{\mp}$$

$$\langle | +\tfrac{1}{2} \mp \tfrac{1}{2} \rangle \langle +\tfrac{1}{2} \pm \tfrac{1}{2} | \rangle = \frac{\mp i}{\sqrt{2}}\,\phi_{\pm 1}^1(01) \pm \frac{1}{\sqrt{2}}\,\chi_{\pm 1}^{\mp}$$

$$\langle | \mp\tfrac{1}{2} - \tfrac{1}{2} \rangle \langle \pm\tfrac{1}{2} - \tfrac{1}{2} | \rangle = \frac{\mp i}{\sqrt{2}}\,\phi_{\pm 1}^1(10) \mp \frac{1}{\sqrt{2}}\,\chi_{\pm 1}^{\pm}$$

$$\langle | \mp\tfrac{1}{2} + \tfrac{1}{2} \rangle \langle \pm\tfrac{1}{2} + \tfrac{1}{2} | \rangle = \frac{\mp i}{\sqrt{2}}\,\phi_{\pm 1}^1(10) \pm \frac{1}{\sqrt{2}}\,\chi_{\pm 1}^{\pm}$$

Double quantum $q = 2$

$$\langle | \mp\tfrac{1}{2} \mp \tfrac{1}{2} \rangle \langle \pm\tfrac{1}{2} \pm \tfrac{1}{2} | \rangle = -\phi_{\pm 2}^2(11)$$

where $\chi_q^{\pm} = \pm \frac{1}{\sqrt{2}}\,(\phi_q^1(11) \pm \phi_q^2(11))$, $q = \pm 1$ only

Using these ideas to replace the two spin operator basis $|m_1 m_2\rangle\langle m'_1 m'_2|$ of (2) by the multipole expansion, the spin density operator becomes [14],

$$\sigma(t) = \sum_{\substack{kq\\k1k2}} \phi_q^k(k_1 k_2)[t]\,T^{kq}(k_1 k_2), \tag{5}$$

where $\phi_q^k(k_1 k_2)$ are the various multipole polarizations,

$$\phi_q^k(k_1 k_2)[t] = \mathrm{Tr}\{\sigma(t) T_q^k(k_1 k_2)\} \tag{6}$$

which uses the orthogonality properties of the operators [14]. The relation between the transition probabilities and the ϕs is

$$\sigma_{m_1 m_2}^{m_1' m_2'}(t) = \sum_{\substack{kqq_1q_2\\k1k2}} (i)^{k_1+k_2}\sqrt{[(2k+1)(2k_1+1)(2k_2+1)]}\begin{pmatrix} k & k_1 & k_2\\ -q & q_1 & q_2\end{pmatrix}\begin{pmatrix} I_1 & k_1 & I_1\\ -m_1 & q_1 & m'_1\end{pmatrix}$$

$$\times (-1)^{I_1+I_2+k_1-k_2-q-m_1-m_2}\begin{pmatrix} I_2 & k_2 & I_2\\ -m_2 & q_2 & m'_2\end{pmatrix}\phi_q^k(k_1 k_2)[t]. \tag{7}$$

Table 2 lists all 16 transition probabilities for the two spin 1/2 case. Table 3 gives

Table 3. Tensorial interpretation of the 2 spin-1/2 multipole operator basis.

Polarization	Multipole operator	Spin operator	Name	No. of components
1	1	E	Identity	1
$\phi_0^0(11)$	$\langle T_0^0(11)\rangle$	$\mathbf{I}_1\cdot\mathbf{I}_2$	Dot product	1
$\phi_q^1(10)$	$\langle T_q^1(10)\rangle$	$\mathbf{I}_1$	Spin one	3
$\phi_q^1(01)$	$\langle T_q^1(01)\rangle$	$\mathbf{I}_2$	Spin two	3
$\phi_q^1(11)$	$\langle T_q^1(11)\rangle$	$\mathbf{I}_1\times\mathbf{I}_2$	Cross product	3
$\phi_q^2(11)$	$\langle T_q^2(11)\rangle$	$[\mathbf{I}_1\ \mathbf{I}_2]^{(2)}$	Second rank tensor	5

Table 4. Hilbert space representation of 2 spin-1/2 multipole operator basis in the order $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$, $|\beta\beta\rangle$.

$$T^{00}(00) = 1/2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad T^{00}(11) = 1/\sqrt{12} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$T^{11}(01) = -i/\sqrt{2} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad T^{10}(01) = -i/2 \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$T^{11}(10) = -i/\sqrt{2} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad T^{10}(10) = -i/2 \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$T^{11}(11) = 1/2 \begin{pmatrix} 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad T^{10}(11) = 1/\sqrt{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$T^{22}(11) = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad T^{21}(11) = 1/2 \begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$T^{20}(11) = 1/\sqrt{6} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

the tensor interpretation while table 4 gives the matrix representation of each multipole operator. In table 2, for the single quantum processes, the following definition is used [1]

$$\chi_q^{\pm} = \frac{\pm 1}{\sqrt{2}} (\phi_q^1(11) \pm \phi_q^2(11)), \tag{8}$$

for $q = \pm 1$ only.

In conventional N.M.R. it is only possible to measure the xy components of spin 1 or spin 2 given respectively by $\phi^1_{\pm 1}(10)$ and $\phi^1_{\pm 1}(01)$. The other quantities require different experimental arrangements, which from table 2 can be related to the appropriate transitions. The vector cross product plays an important role in spin coupling and decoupling.

2.2. *Hamiltonians*

The spin dynamics of two spins of 1/2 is determined by the hamiltonian

$$\mathscr{H}_0/\hbar = (-\gamma_1 I_{1z} - \gamma_2 I_{2z})B_0 + J\mathbf{I}_1\cdot\mathbf{I}_2, \tag{9}$$

$$= i\omega_{01}T^{10}(10) + i\omega_{02}T^{10}(01) + \sqrt{\tfrac{3}{2}}JT^{00}(11), \tag{10}$$

valid when no r.f. field is on and where the second line shows that the hamiltonian can be expressed naturally in the multipole form. The rf is treated in the following paper [1]. Note that in this basis $T^{00}(11)\mathbf{I}_1\cdot\mathbf{I}_2$ occurs naturally whereas the truncated form,

$$I_{1z}I_{2z} \propto \frac{2}{\sqrt{3}}\,T^{20}(11) - \frac{1}{\sqrt{3}}\,T^{00}(11) \tag{11}$$

involves more terms and is not natural to use.

3. Two coupled spins of 1/2

The hamiltonian (10) leads to well known results for the dipole allowed spin transition [18], the spin dynamics are usually calculated from an initial polarization $I_{1z}(0)$, (Heisenberg picture). In this section a variety of different initial preparations of the state, derived from the previous history produced by pulse sequences, is included. In the Liouville approach used here the eigenvalues are the observable multiquantum frequencies. The eigenfunctions give various weights to the different initial conditions, $\phi^k_q(k_1k_2)[0]$. The determining set of differential equations resulting from $\mathscr{H}_0$ are

$$\frac{d\phi^0_0(11)}{dt} = i\sqrt{\tfrac{8}{3}}\,\omega_D\,\phi^1_0(11), \tag{12}$$

$$\frac{d\phi^1_q(10)}{dt} = iq\omega_{01}\phi^1_q(10) + \frac{J}{\sqrt{2}}\,\phi^1_q(11), \tag{13}$$

$$\frac{d\phi^1_q(01)}{dt} = iq\omega_{02}\,\phi^1_q(01) - \frac{J}{\sqrt{2}}\,\phi^1_q(11), \tag{14}$$

$$\frac{d\phi^1_q(11)}{dt} = i\sqrt{\tfrac{8}{3}}\,\omega_D\,\phi^0_0(11)\,\delta_{q0} + iq\bar{\omega}\phi^1_q(11) + i\omega_D\,\frac{(4-q^2)^{1/2}}{\sqrt{3}}\,\phi^2_q(11)$$
$$+ \frac{J}{\sqrt{2}}\,(\phi^1_q(01) - \phi^1_q(10)). \tag{15}$$

$$\frac{d\phi^2_q(11)}{dt} = \frac{i\omega_D(4-q^2)^{1/2}}{\sqrt{3}}\,\phi^1_q(11) + iq\bar{\omega}\phi^2_q(11), \tag{16}$$

where

$$\omega_D = \tfrac{1}{2}(\omega_{01} - \omega_{02}) \tag{17}$$

and

$$\bar{\omega} = \tfrac{1}{2}(\omega_{01} + \omega_{02}). \tag{18}$$

The details of this derivation are given in Appendix *B*. Referring to table 3, the observable magnetization depends for spins 1 and 2 respectively on the time dependence of $\phi^1_{\pm 1}(10)$ and $\phi^1_{\pm 1}(01)$. The transition probabilities depend upon all the polarizations (table 2) even though only $\phi^1_{\pm 1}(10)$ and $\phi^1_{\pm 1}(01)$ are the polarizations detected in N.M.R.

Immediately from (13) and (14) it is seen that the spin polarization for spin 1 and 2 do not couple directly, but via $\phi^1_q(11)$, i.e. the cross product. In fact, if the first spin is being observed, the formal solution for spin 1 is,

$$\phi^1_q(10)[t] = \exp[iq\omega_{01}t]\phi^1_q(10)[0] + \frac{J}{\sqrt{2}}\int_0^t \exp[i(t-t')q\omega_{01}]\phi^1_q(11)[t']\,dt'. \tag{19}$$

Clearly if $\phi^1_q(11)[t]$ can be made to vanish, the time dependence of $\phi^1_q(10)[t]$ is simple precession with frequency ω_{01}. The splitting of this resonance results only from the cross product. The same argument applies to spin 2. Equation (19) is the starting point for understanding spin coupling and decoupling.

The set of equations (12)–(16) are now solved exactly from arbitrary initial conditions. The 15 equations block out into two 1×1, for $q = \pm 2$; two 4×4s for $q = \pm 1$; and one 5×5 for $q = 0$. The solutions of these give the dynamics of the double, single and zero quantum processes.

3.1. *Double quantum processes; $q = \pm 2$*

Only one term with quadrupole character, $\phi^2_{\pm 2}(11)$ exists; the spin magnitude I has no influence on this term. The solution,

$$\phi^2_{\pm 2}(11)[t] = \exp[\pm i2\bar{\omega}t]\phi^2_{\pm 2}(11)[0] \tag{20}$$

requires the initial production of double quantum polarization in order to observe this coherence. A variety of 2 pulse sequences (2-D spectroscopy) allows indirect detection of this which has the advantage of being unsplit permitting chemical shifts to be easily measured.

3.2. *Single quantum processes; $q = \pm 1$*

From (13)–(16) the determining set of equations take the form,

$$\frac{d}{dt}\begin{pmatrix}\hat{\phi}^1_{\pm 1}(10)[t]\\ \hat{\phi}^1_{\pm 1}(01)[t]\\ \hat{\phi}^1_{\pm 1}(11)[t]\\ \hat{\phi}^2_{\pm 1}(11)[t]\end{pmatrix} = i\begin{pmatrix}\pm\omega_D & 0 & -iJ/\sqrt{2} & 0\\ 0 & \mp\omega_D & iJ/\sqrt{2} & 0\\ iJ/\sqrt{2} & -iJ/\sqrt{2} & 0 & \omega_D\\ 0 & 0 & \omega_D & 0\end{pmatrix}\begin{pmatrix}\hat{\phi}^1_{\pm 1}(10)[t]\\ \hat{\phi}^1_{\pm 1}(01)[t]\\ \hat{\phi}^1_{\pm 1}(11)[t]\\ \hat{\phi}^2_{\pm 1}(11)[t]\end{pmatrix}, \tag{21}$$

where the rotating frame is (see (18))

$$\hat{\phi}^k_q(k_1k_2)[t] = \exp[-i\bar{\omega}qt]\phi^k_q(k_1k_2). \tag{22}$$

The four eigenfrequencies are

$$\left.\begin{aligned}\lambda_{\pm 2} &= \pm\frac{J}{2}\pm\frac{1}{2}D,\\ \lambda_{\pm 1} &= \mp\frac{J}{2}\pm\frac{1}{2}D,\end{aligned}\right\} \tag{23}$$

where

$$D = \sqrt{(4\omega_{\mathrm{D}}^2 + J^2)}, \tag{24}$$

which give the well known single quantum spectrum of four lines (18). The four eigenvectors of the matrix are

$$\Xi_{\pm i} = \frac{1}{2(\omega_{\mathrm{D}}^2 + \lambda_i^2)^{1/2}}\begin{pmatrix} i(\omega_{\mathrm{D}} \pm \lambda_i) \\ i(\omega_{\mathrm{D}} \mp \lambda_i) \\ \sqrt{2}\,(\omega_{\mathrm{D}}^2 - \lambda_i^2)/J \\ \dfrac{\pm\sqrt{2}\,\omega_{\mathrm{D}}(\omega_{\mathrm{D}}^2 - \lambda_i^2)}{J\lambda_i}\end{pmatrix} \tag{25}$$

for $i = 1$ and 2. The matrix of eigenfunctions,

$$\underline{\underline{\Xi}} = (\Xi_2, \Xi_1, \Xi_{-1}, \Xi_{-2}) \tag{26}$$

diagonalizes (25), permitting the solution to be found. The result is

$$\begin{pmatrix} \hat{\phi}^1_{+1}(10)[t] \\ \hat{\phi}^1_{+1}(01)[t] \\ \hat{\phi}^1_{+1}(11)[t] \\ \hat{\phi}^2_{+1}(11)[t] \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{12} & M_{11}^* & -M_{13}^* & M_{14}^* \\ -M_{13} & M_{13}^* & M_{33} & M_{34} \\ -M_{14} & -M_{14}^* & M_{34} & M_{44} \end{pmatrix}\begin{pmatrix} \phi^1_{+1}(10)[0] \\ \phi^1_{+1}(01)[0] \\ \phi^1_{+1}(11)[0] \\ \phi^2_{+1}(11)[0] \end{pmatrix}. \tag{27}$$

Table 5 gives the seven distinct matrix entries. The $q = -1$ solutions are found from the symmetry

$$\phi^k_q(k_1k_2)^* = (-1)^{k-q}\phi^k_{-q}(k_1k_2). \tag{28}$$

There are both dipole and quadrupole character terms [19] which are observed depending upon the initial polarization $\phi^k_q(k_1k_2)[0]$. To obtain the expectation values it is only necessary to specify the initial conditions and compute

$$\langle F\rangle = \mathrm{Tr}\,\{\sigma(t)F\}. \tag{29}$$

Transition probabilities are given by taking $F = |m_1m_2\rangle\langle m_1'm_2'|$, see table 2. Normally it is assumed that the observable is $F = I_{1-} + I_{2-}$, with $\gamma_1 \sim \gamma_2$, or in terms of multipoles,

$$F = I_{1-} + I_{2-} = -i\sqrt{2}\,[T^{1-1}(10) + T^{1-1}(01)], \tag{30}$$

where $I_{i\pm} = I_{ix} \pm iI_{iy}$. From tables (5) and [27, 28],

$$\langle I_{1-} + I_{2-}\rangle[t] = [1 - \sin 2\theta]\cos\lambda_2 t + [1 + \sin 2\theta]\cos\lambda_1 t, \tag{31}$$

Table 5. Single quantum matrix elements of (27).

$$2M^1_{11} = [\cos \lambda_1 t + \cos \lambda_2 t + i \cos 2\theta(\sin \lambda_1 t + \sin \lambda_2 t)]$$

$$2M^1_{12} = \sin 2\theta(\cos \lambda_1 t - \cos \lambda_2 t)$$

$$2M^1_{13} = -\frac{1}{\sqrt{2}}[(1 - \sin 2\theta) \sin \lambda_1 t - (1 + \sin 2\theta) \sin \lambda_2 t - i \cos 2\theta(\cos \lambda_1 t - \cos \lambda_2 t)]$$

$$2M^1_{14} = -\frac{1}{\sqrt{2}}[(1 + \sin 2\theta) \sin \lambda_1 t - (1 - \sin 2\theta) \sin \lambda_2 t - i \cos 2\theta(\cos \lambda_1 t - \cos \lambda_2 t)]$$

$$2M^1_{33} = [(1 - \sin 2\theta) \cos \lambda_1 t + (1 + \sin 2\theta) \cos \lambda_2 t]$$

$$2M^1_{44} = [(1 + \sin 2\theta) \cos \lambda_1 t + (1 - \sin 2\theta) \cos \lambda_2 t]$$

$$2M^1_{34} = i \cos 2\theta(\sin \lambda_1 t + \sin \lambda_2 t)$$

relations

$$\sin 2\theta = J/D = \frac{-(\omega_D^2 - \lambda_2^2)}{(\omega_D^2 + \lambda_2^2)} = \frac{(\omega_D^2 - \lambda_1^2)}{(\omega_D^2 + \lambda_1^2)}$$

$$\cos 2\theta = 2\omega_D/D = \mp 2\lambda_i \omega_D/(\omega_D^2 + \lambda_i^2)$$

$$(\omega_D^2 - \lambda_{\pm 2}^2) = \mp J\lambda_{\pm 2}$$

$$(\omega_D^2 - \lambda_{\pm 1}^2) = \pm J\lambda_{\pm 1}$$

$$D = \sqrt{(4\omega_D^2 + J^2)}$$

with the assumption that the initial conditions are normalized to $\phi^1_{-1}(10)[0] = \phi^1_{-1}(01)[0] = i/\sqrt{2}$. This result gives the well known relative intensities for the four frequencies when $\gamma_1 \sim \gamma_2$. The spectrum is found by Fourier transforming (31) which, as it stands, represents the free induction decay (if relaxation were included).

Consider the case that spin 2 is the observed spin, and only it is initially polarized, (the argument is identical for spin 1). From (27) and table 5 one obtains

$$\phi^1_1(01)[t] = \tfrac{1}{4}[\exp(-i\lambda_1 t)(1 + \cos 2\theta) + \exp(-i\lambda_2 t)(1 + \cos 2\theta) + \exp(i\lambda_1 t)(1 - \cos 2\theta) + \exp(i\lambda_2 t)(1 - \cos 2\theta)]\phi^1_1(01)[0] \quad (32)$$

thereby showing that the J coupling causes a transfer of polarization from spin 2 lines (at $-\lambda_1$, $-\lambda_2$) to the frequency positions of spin 1 (at $+\lambda_1$, $+\lambda_2$).

On the other hand, a variety of pulses can produce differing initial conditions which lead to varying intensities associated with the four spectral lines. These are all given by (27). It is not possible to eliminate the J splitting, however, with any state preparing pulse sequence alone, although inspection of (27) shows that it is possible to transfer coherence between lines in analogy with, for example experiments on a single quadrupole-split $I = 1$ spin [3, 20]. For spins of 1/2, polarization transfer is essential for increasing spectral intensities in many practical applications.

3.3. *Zero quantum processes*, $q = 0$

From (12)–(16) it follows that for the zero quantum processes, $q = 0$, there is one five by five matrix coupling together the five zero quantum processes,

$$\frac{d}{dt}\begin{pmatrix} \phi_0^0(11)[t] \\ \phi_0^1(11)[t] \\ \phi_0^2(11)[t] \\ \phi_0^1(10)[t] \\ \phi_0^1(01)[t] \end{pmatrix} = i\begin{pmatrix} 0 & \sqrt{\frac{8}{3}}\,\omega_D & 0 & 0 & 0 \\ \sqrt{\frac{8}{3}}\,\omega_D & 0 & \frac{2}{\sqrt{3}}\,\omega_D & iJ/\sqrt{2} & -iJ/\sqrt{2} \\ 0 & \frac{2}{\sqrt{3}}\,\omega_D & 0 & 0 & 0 \\ 0 & -iJ/\sqrt{2} & 0 & 0 & 0 \\ 0 & iJ/\sqrt{2} & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \phi_0^0(11)[t] \\ \phi_0^1(11)[t] \\ \phi_0^2(11)[t] \\ \phi_0^1(10)[t] \\ \phi_0^1(01)[t] \end{pmatrix}. \tag{33}$$

The eigenfrequencies are found to be

$$\lambda = \pm D,\ 0,\ 0,\ 0, \tag{34}$$

with D defined by (24).

The solutions are

$$\begin{pmatrix} \phi_0^0(11)[t] \\ \phi_0^1(11)[t] \\ \phi_0^2(11)[t] \\ \phi_0^1(10)[t] \\ \phi_0^1(01)[t] \end{pmatrix} = \begin{pmatrix} M_{11}^\circ & M_{12}^\circ & M_{13}^\circ & M_{14}^\circ & -M_{14}^\circ \\ M_{12}^\circ & M_{22}^\circ & M_{23}^\circ & M_{24}^\circ & -M_{24}^\circ \\ M_{13}^\circ & M_{23}^\circ & M_{33}^\circ & M_{34}^\circ & -M_{34}^\circ \\ -M_{14}^\circ & -M_{24}^\circ & -M_{34}^\circ & M_{44}^\circ & M_{45}^\circ \\ M_{14}^\circ & M_{24}^\circ & M_{34}^\circ & M_{45}^\circ & M_{44}^\circ \end{pmatrix}\begin{pmatrix} \phi_0^0(11)[0] \\ \phi_0^1(11)[0] \\ \phi_0^2(11)[0] \\ \phi_0^1(10)[0] \\ \phi_0^1(01)[0] \end{pmatrix}, \tag{35}$$

with the matrix elements given in table (6).

Table 6. Zero quantum matrix elements of (35).

$M_{11}^\circ = [1 - 2/3\cos^2 2\theta(1 - \cos Dt)]$
$M_{12}^\circ = i\sqrt{(2/3)}\cos 2\theta \sin Dt$
$M_{13}^\circ = -\frac{\sqrt{2}}{3}\cos^2 2\theta(1 - \text{cps } Dt)$
$M_{14}^\circ = -i/\sqrt{3}\sin 2\theta\cos 2\theta(1 - \cos Dt)$
$M_{22}^\circ = \cos Dt$
$M_{23}^\circ = i/\sqrt{3}\cos 2\theta \sin Dt$
$M_{24}^\circ = -\frac{\sin 2\theta}{\sqrt{2}}\sin Dt$
$M_{33}^\circ = \left[1 - \frac{\cos^2 2\theta}{3}(1 - \cos Dt)\right]$
$M_{34}^\circ = -\frac{i\cos 2\theta \sin 2\theta}{\sqrt{6}}(1 - \cos Dt)$
$M_{44}^\circ = \left[1 - \frac{\sin^2 2\theta}{2}(1 - \cos Dt)\right]$
$M_{45}^\circ = 1/2\sin^2 2\theta(1 - \cos Dt)$

These equations give the exact time dependence of the zero quantum process from any initial condition, $\phi_0^k(k_1k_2)[0]$. For $|J| \ll |\omega_D|$, it is seen that the 3 bilinear operators $\phi_0^0(11)$, $\phi_0^1(11)$, and $\phi_0^2(11)$ uncouple from the magnetization of spins 1 and 2 (i.e. $\phi_0^0(10)$, $\phi_0^1(01)$). In this case, $\phi_0^1(10)$ and $\phi_0^1(01)$ are constants, while the two spin operators $\phi_0^k(11)$ oscillate with two frequencies $\pm 2\omega_D$.

4. Pathway of spin coupling

From (21) and (19) it is evident that the observed spectral splitting does not occur from a direct coupling of the spin vector operators $\mathbf{I}_1$ and $\mathbf{I}_2$. Rather the operator $T^{1q}(11) \propto \mathbf{I}_1 \times \mathbf{I}_2$ provides the means through which polarization can be transferred between $\phi_q^1(10)$ and $\phi_q^1(01)$.

Viewed from the $\bar{\omega}$ frame the exact equations can be written

$$\frac{d}{dt}\,\hat{\phi}_q^1(01) = -iq\omega_D\,\hat{\phi}_q^1(01) - \frac{J}{2}\,(\hat{\chi}_q^+ - \hat{\chi}_q^-), \tag{36}$$

$$\frac{d}{dt}\,\hat{\phi}_q^1(10) = iq\omega_D\,\hat{\phi}_q^1(10) + \frac{J}{2}\,(\hat{\chi}_q^+ - \hat{\chi}_q^-). \tag{37}$$

The J terms can be thought of as producing friction between $\hat{\phi}_q^1(01)$ and $\hat{\phi}_q^1(10)$ via $\hat{\chi}_q^+ - \hat{\chi}_q^-$. If it were not for the $\hat{\chi}$ terms, the spins would be uncoupled and precess at $\pm\omega_D$ in the $\bar{\omega}$ frame. The reason that the cross product polarization, $\hat{\phi}_q^1(11)$ is replaced by the $\hat{\chi}_q^\pm$ terms is that the latter have, for negligible J, eigenfrequencies of $\pm\omega_D$ as shown from the exact equation

$$\frac{d}{dt}\,\hat{\chi}_q^\pm = \pm i\omega_D\,\hat{\chi}_q^\pm \mathop{}_{+}^{-} \frac{J}{2}\,[\hat{\phi}_q^1(10) - \hat{\phi}_q^1(01)]. \tag{38}$$

Both the single spin (36)–(37) and the bilinear operators (38) have oscillations which are in-phase, and these are coupled via J to each other. In the limit of small J; $|\omega_D| \gg |J|/2$, the following terms couple degenerately,

$$\phi_1^1(10) \text{ to } \chi_1^-; \tag{39 a}$$

$$\phi_{-1}^1(10) \text{ to } \chi_{-1}^+; \tag{39 b}$$

$$\phi_1^1(01) \text{ to } \chi_1^+; \tag{39 c}$$

and

$$\phi_{-1}^1(01) \text{ to } \chi_{-1}^-. \tag{39 d}$$

The corresponding eigenfrequencies are $\pm(\omega_D \pm J/2)$ in agreement with the small J limit in (23). Degenerate perturbation theory is thus equivalent to truncating the hamiltonian to $JI_{1z}I_{2z}$.

The multipole theory of spin coupling reveals, therefore, the pathway through which the two spins can communicate. It is a vector quantity $\mathbf{I}_1 \times \mathbf{I}_2$, perpendicular to both $\mathbf{I}_1$ and $\mathbf{I}_2$, which oscillates in the $\bar{\omega}$ frame at $\pm\omega_D$ or in the laboratory frame at ω_{01} and ω_{02}. The ω_{01} component is degenerately coupled to spin 1 while the ω_{02} component is degenerately coupled to spin 2. Equation (27) and table 5 gives the solution in the small J limit, i.e. $\cos 2\theta \approx 1$ and $\sin 2\theta \approx 0$.

This pathway is given by those multilinear operators which provides a route by which multiquantum coherences can be transferred. A similar idea has recently been discussed by Ernst [21].

Spin coupling can also be visualized in the strong J limit. One method is to use the Laplace transform, [22]

$$\Phi(s) = \int_0^\infty \exp(-st)\phi(t)\,dt \tag{40}$$

of (36)–(38). Solving the resultant set by eliminating $\chi_q^\pm(t)$ gives

$$\left[s + iq\omega_D + \frac{J^2}{2}\cdot\frac{s}{s^2+\omega_D^2}\right]\Phi_q^1(01)[s] = \phi_q^1(01)[0] + \frac{J^2}{2}\cdot\frac{s}{s^2+\omega_D^2}\,\Phi_q^1(10)[s] - \frac{J}{2}\left[\frac{1}{s-i\omega_D}\,\hat{\chi}_q^+[0] - \frac{1}{s+i\omega_D}\,\hat{\chi}_q^-[0]\right] \tag{41}$$

and

$$\left[s - iq\omega_D + \frac{J^2}{2}\cdot\frac{s}{s^2+\omega_D^2}\right]\Phi_q^1(10)[s] = \phi_q^1(10)[0] + \frac{J^2}{2}\cdot\frac{s}{s^2+\omega_D^2}\,\Phi_q^1(01)[s] + \frac{J}{2}\left[\frac{1}{s-i\omega_D}\,\hat{\chi}_q^+[0] - \frac{1}{s+i\omega_D}\,\hat{\chi}_q^-[0]\right]. \tag{42}$$

Initial values are $\phi_q^1(ij)[0]$ and $\chi_q^\pm[0]$. Note that $\phi_q^1(10)$ depends on $\phi_q^1(01)$ and *vice versa*. Eliminating one gives, say for spin 2,

$$\Phi_q^1(01)[s] = \frac{1}{R(s)}\left[\{(s^2+\omega_D^2)(s-iq\omega_D) + J^2 s/2\}\phi_q^1(01)[0] + \frac{J^2 s}{2}\,\phi_q^1(10)[0] - \frac{J}{2}(s^2+\omega_D^2)(s-iq\omega_D) \times\left\{\frac{1}{s-i\omega_D}\,\hat{\chi}_q^+[0] - \frac{1}{s+i\omega_D}\,\hat{\chi}_q^-[0]\right\}\right], \tag{43}$$

where the resolvent is

$$R(s) = (s^2+\omega_D^2)^2 + J^2 s^2. \tag{44}$$

The four roots are identical to (23) and the inverse of (43) reproduces $\phi_q^1(01)[t]$ of (27).

This solution shows that no new pathway occurs for strong coupling, but rather highlights the possibility for passing the polarization back and forth between the two spins repeatedly. The degenerate perturbation treatment above allows only one transfer while repeated oscillations will shift the eigenfrequencies,

$$\lambda_i \cong \pm\frac{J}{2} \pm \omega_D\left[1 + \frac{J^2}{\omega_D^2} + \frac{1}{2}\frac{J^4}{\omega_D^4}\cdots\right], \tag{45}$$

which will approach the exact eigenfrequencies, (23), and consequently will modify the eigenfunctions.

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APPENDIX A

Properties of $T^{kq}(k_1 k_2)$

The two spin multipole operators are obtained by taking single spin operators, $\mathscr{Y}^{(k_1)q_1}(\mathbf{I}_1)$ and $\mathscr{Y}^{(k_2)q_2}(\mathbf{I}_2)$, and forming linear combinations according to (4) so that $T^{kq}(k_1 k_2)$ are irreducible under SO(3), [7]. The following properties are general, and are not restricted to I_1 or I_2 being 1/2:

(1) Adjoint

$$T^{kq}(k_1 k_2)^\dagger = (-1)^{k-q} T^{k-q}(k_1 k_2) \equiv T_q^k(k_1 k_2). \tag{A 1}$$

(2) Orthonormalization

$$\langle\langle T^{kq}(k_1 k_2) \,|\, T^{k'q'}(k_1' k_2') \rangle\rangle \equiv \mathrm{Tr}\{T^{kq}(k_1 k_2)^\dagger T^{k'q'}(k_1' k_2')\} = \delta_{kk'}\, \delta_{qq'}\, \delta_{k_1 k_1'}\, \delta_{k_2 k_2'}. \tag{A 2}$$

(3) Wigner–Eckart theorem, for a tensor operator F^{lm}

$$\langle\langle T^{kq}(k_1 k_2) \,|\, F^{lm} \,|\, T^{k'q'}(k_1' k_2') \rangle\rangle = (-1)^{k-q} \begin{pmatrix} k & l & k' \\ -q & m & q' \end{pmatrix} \langle\langle T^{k}(k_1 k_2) \,||\, F^{l} \,||\, T^{k'}(k_1' k_2') \rangle\rangle \tag{A 3}$$

where $\langle\langle T \,||\, F \,||\, T \rangle\rangle$ are reduced matrix elements and

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

is a $3-j$ coefficient.

(4) Reduced matrix elements when F^{lm} is a commutator superoperator with some operator B:

(*a*) When $F^l = [T^l(l0), B] \equiv \mathscr{L}^l(\mathbf{I}_1)$

$$\langle\langle T^{k}(k_1 k_2) \,||\, \mathscr{L}^l(l0) \,||\, T^{k'}(k_1' k_2') \rangle\rangle = 2\phi(k_1 l k_1')\, \delta_{k_2 k_2'} (-1)^{k_1' + k_2' + k'} \times \sqrt{\frac{(2k+1)(2k'+1)(2k_1'+1)}{(2I_1+1)(2I_2+1)}} \begin{Bmatrix} k_1 & k_1' & l \\ k' & k & k_2 \end{Bmatrix} a_{I_1}^{l k_1 k_1'}. \tag{A 4}$$

(*b*) When $F^l = [T^l(0l), B] = \mathscr{L}^l(\mathbf{I}_2)$

$$\langle\langle T^{k}(k_1 k_2) \,||\, \mathscr{L}^l(\mathbf{I}_2) \,||\, T^{k'}(k_1' k_2') \rangle\rangle = 2\phi(k_2 l k_2')\, \delta_{k_1 k_1'} (-1)^{k_1 + k_2 + k} \times \sqrt{\frac{(2k+1)(2k'+1)(2k_2'+1)}{(2I_1+1)(2I_2+1)}} \begin{Bmatrix} k_2 & k_2' & l \\ k' & k & k_1 \end{Bmatrix} a_{I_2}^{l k_2 k_2'}, \tag{A 5}$$

where $\phi(l_1 l_2 l_3)$ is 1 if $l_1 + l_2 + l_3$ is odd and zero otherwise and

$$a_{I_i}^{l k_i k_i'} = (i)^{k_i' + l + k_i} [(2l+1)(2k_i+1)(2I_i+1)]^{1/2} (-1)^{2I_i} \begin{Bmatrix} k_i' & l & k_i \\ I_i & I_i & I_i \end{Bmatrix}. \tag{A 6}$$

The quantities $\{\because\}$ are $6-j$ coefficients.

(*c*) When $F = [T^{lm}(l_1 l_2), B]_- = \mathscr{L}^{lm}(l_1 l_2)B$,

$$\langle\langle T^{kq}(k_1 k_2) | \mathscr{L}^{lm}(l_1 l_2) | T^{k'q'}(k_1' k_2')\rangle\rangle = 2[(l)(k)(k')(l_1)(k_1)(k_1') \times (l_2)(k_2)(k_2')]^{1/2}(-1)^{k-q}\begin{pmatrix} k & l & k' \\ -q & m & q' \end{pmatrix}(-1)^{l+k+k'+2(I_1+I_2)} \times (i)^{l_1+k_1+k_1'+l_2+k_2+k_2'}\begin{Bmatrix} k_1 & l_1 & k_1' \\ I_1 & I_1 & I_1 \end{Bmatrix}\begin{Bmatrix} k_2 & l_2 & k_2' \\ I_2 & I_2 & I_2 \end{Bmatrix} \times \begin{Bmatrix} l & k' & k \\ l_1 & k_1' & k_1 \\ l_2 & k_2' & k_2 \end{Bmatrix}[\phi(k_1 l_1 k_1') + (-1)^{l_1+k_1+k_1'}\phi(k_2 l_2 k_2')], \quad (A\,7)$$

which involves a $9-j$ coefficient. The notation $(l) \equiv 2l + 1$ is used to compact the expression.

Appendix B

Derivation of (16) to (22)

Substitution of (5) and (10) into the quantum Liouville equation

$$i\hbar \frac{\partial \sigma}{\partial t} = [\mathscr{H}_0, \sigma]$$

and taking the trace, (A 1) leads directly to

$$\frac{\partial \phi_q^k(k_1 k_2)}{\partial t} = -\sum_{k' k_1' k_2'} \Bigg\{ \omega_{01}(-1)^{k-q}\begin{pmatrix} k & 1 & k' \\ -q & 0 & q \end{pmatrix} \times \langle\langle T^k(k_1 k_2) || \mathscr{L}^1(\mathbf{I}_1) || T^{k'}(k_1' k_2)\rangle\rangle\, \delta_{k_2 k_2'} + \omega_{02}(-1)^{k-q}\begin{pmatrix} k & 1 & k' \\ -q & 0 & q \end{pmatrix}\langle\langle T^k k_1 k_2 || \mathscr{L}^1(\mathbf{I}_2) || T^{k'}(k_1 k_2')\rangle\rangle\, \delta_{k_1 k_1'} - i\frac{\sqrt{3}\,J}{2}\langle\langle T^{kq}(k_1 k_2) | \mathscr{L}^{00}(11) | T^{k'q}(k_1' k_2')\rangle\rangle \Bigg\} \phi_q^{k'}(k_1' k_2'). \quad (A\,8)$$

Specializing to $I_1 = I_2 = 1/2$ in (A 4)–(A 7) and using appropriate kqk_1k_2s reduces the above equation to (12)–(16).

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