

Notes on Spin Operators

K. A. Earle

Physics Department, University at Albany (SUNY)

1400 Washington Ave., Albany, NY 12222

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Abstract

The spin operator basis set is a useful tool to facilitate spectroscopic lineshape computations that use a density matrix approach, such as the stochastic Liouville equation. For systems with multiple, coupled spins, a generalization of the Wigner-Eckart theorem allows a concise formulation of the spin dynamics. This concision is achieved by the use of a spin basis set in which the coupled spins are represented by an orthonormal set related to Irreducible Spherical Tensor Operators. Two important cases are considered. The first case is an electron (spin S) coupled to a single nucleus (spin I). This case is chosen to facilitate comparison to the uncoupled representation commonly employed in EPR spectral lineshape computations. The second case considered is that of two paramagnetic centers each coupled to a nearby nucleus, for a total of four spins. This case is relevant for macromolecules labeled with two nitroxide spin labels, or other paramagnetic centers interacting via dipole-dipole couplings. The results of these calculations may be conveniently expressed in terms of Wigner $3j$, $6j$ and $9j$ symbols, for which accurate and efficient methods of computation exist.

1 Introduction

Density matrix methods play an important role in the computation of spin dynamics. For systems that can be described by only one or two relevant spins, it is a straightforward, though tedious, exercise to work with the spin operators directly in an uncoupled basis. This is the approach taken by, *e.g.*, Freed and co-workers in their classic analysis of the EPR lineshape problem. [1] In that calculation, angular momentum theory was used to systematize and organize those aspects of the computation involving spatial degrees of freedom for the relevant relaxation mechanism, rotational diffusion. The relevant basis set describing the spin operators in transition (or Liouville) space utilized a direct product or uncoupled representation and did not take advantage of the precision and economy of notation achievable by representing the spin basis set in terms of Irreducible Spherical Tensor Operators (ISTO's). Nevertheless, the expressions for

the matrix elements that one derives in the uncoupled basis are extremely useful and have been applied to the analysis of a wide variety of systems over the years. Recent reviews of applications of these methods to the high field EPR case are available elsewhere. [2, 3]

Although the bottom-up approach developed by Freed and co-workers is constructive and useful, extensions of the formalism require recomputation from scratch. Examination of the expressions for the relevant matrix elements [1, 4] may convince the reader that a more general, top-down approach would be valuable for extensions of the theory to situations of greater complexity, although it should be stressed that results obtained *via* different methods must be equivalent physically. The question is, rather, one of the *insights* that one may obtain by comparison of different approaches. In addition, the proper choice of basis set can reduce the computational burden, as a basis that is a more faithful representation of the underlying spin dynamics will lead to smaller matrix representations of the relevant equations of motion

Since Racah's pioneering work in the 40's on the theory of complex spectra, tensor operator methods have become an increasingly indispensable tool for the study of spin dynamics. Just as Judd's classic text on operator techniques [5] made the insights of Racah and others more accessible to atomic spectroscopists, the book by Blum [6] indicated the possibilities for applications of tensor operator techniques in the study of spin dynamics. In the journal literature, Benetis has applied these notions to a variety of systems of particular relevance for magnetic resonance. The work presented here will make heavy use of [7]. Kruk [8] provides further examples of the methodology employed here in copious detail.

2 Orthonormal Q operators

In [7], Benetis uses the following operator to represent transitions in spin space

$$Q^{(\Sigma, \sigma)}(S) = (-1)^{S+\sigma} [\Sigma]^{1/2} \sum_n (-1)^{-n} \begin{pmatrix} S & S & \Sigma \\ n + \sigma & -n & -\sigma \end{pmatrix} |S, n + \sigma\rangle \langle S, n| \quad (1)$$

$$\equiv (-1)^{S+\sigma} [\Sigma]^{1/2} \sum_{n, n''} (-1)^{-n} \begin{pmatrix} S & S & \Sigma \\ n'' & -n & -\sigma \end{pmatrix} |S, n''\rangle \langle S, n|, \quad (2)$$

where $[\Sigma] = 2\Sigma + 1$ and implicit use is made of the property of Wigner 3j symbols that the sum of the lower indices (azimuthal quantum numbers) is zero. The index n in Equation 1 may be related to the q index introduced by Freed and coworkers. [1] One finds $n = 2q$. In addition, the p index introduced by Freed and coworkers is equivalent to the σ index in Equations 1 and 2. The form of Q given in Equation 2 is useful for computations involving coupled spins. The Q operators may be rewritten in terms of, *e.g.*, raising and lowering operators when $n \neq n''$. If $n = n''$, the Q operators can represent populations, or population differences.

The Q operators satisfy the following orthonormality relation under the Frobenius trace metric

$$\text{Tr} \left\{ \left(Q^{(\Sigma', \sigma')}(S) \right)^\dagger Q^{(\Sigma, \sigma)}(S) \right\} = \delta_{\Sigma', \Sigma} \delta_{\sigma, \sigma'}. \quad (3)$$

For example, for a single electron spin, the relevant values of Σ are $\Sigma = 1, 0$, corresponding to the four operators $Q^{(1,1)}(S) \propto S_+$, $Q^{(1,0)}(S) \propto S_z$, $Q^{(1,-1)}(S) \propto S_-$ and $Q^{(0,0)}(S) \propto E_S$, where S_\pm and S_z are the standard angular momentum operators, and E_S is the $(2S+1) \times (2S+1)$ identity matrix. In order to prove the orthonormality relation, the identities given in the appendix are useful. Note that the total number of operators in $\{Q\}$ is $(2S+1)^2$, which is the number required to represent all elements of a $(2S+1) \times (2S+1)$ density matrix. Constraints on the density matrix will reduce the number of independent components. The operator $Q^{(0,0)}$, for example, is proportional to the identity matrix E_S and only couples to the dynamics in cases where the total population is a time-dependent quantity. This is the case, for example, in photo-excited triplet EPR. Although such processes will not be discussed here, it is reassuring that the Q operator formalism is sufficiently general to handle this case as well.

The Q operators are related to the standard (unnormalized) ISTO's by a suitably defined reduced matrix element. For $\Sigma = 0, 1, 2$, for example, [8]

$$T^{(0, \sigma)}(S) = \sqrt{(2S+1)} Q^{(0, \sigma)}(S) \quad (4)$$

$$T^{(1, \sigma)}(S) = \sqrt{\frac{S(S+1)(2S+1)}{3}} Q^{(1, \sigma)}(S) \quad (5)$$

$$T^{(2, \sigma)}(S) = \sqrt{\frac{S(S+1)(2S-1)(2S+1)(2S+3)}{30}} Q^{(2, \sigma)}(S). \quad (6)$$

Higher order ISTO's may be constructed from the Q operators by use of the appropriate reduced matrix element. Zare [9] gives reduced matrix elements useful for $0 \leq \Sigma \leq 4$, which can be used provided an additional factor of $1/\sqrt{[\Sigma]}$ is included as has been done implicitly in the expressions given above. In practical applications, $\Sigma = 2$ would be useful for representing the zero field splitting for electrons or the quadrupole interaction for nuclei. In fact, one may define an operator $Q^{(\Xi, \xi)}(I)$ similarly to $Q^{(\Sigma, \sigma)}(S)$ to describe transitions in the I subspace.

3 Two Coupled Spins

When an S spin is coupled to an I spin one may define an appropriate ISTO operator in the coupled spin representation as follows [7]

$$Q^{(\Lambda, \lambda)}(\Sigma, \Xi) = (-1)^{\Sigma - \Xi + \lambda} [\Lambda]^{1/2} \sum_{p, p''} \begin{pmatrix} \Sigma & \Xi & \Lambda \\ p & p'' & -\lambda \end{pmatrix} Q^{(\Sigma, p)}(S) Q^{(\Xi, p'')}(I). \quad (7)$$

These coupled operators span the same $(2S+1)^2 \times (2I+1)^2$ space as the uncoupled operators introduced in previous work. [1, 10] One may express the $Q^{(\Lambda, \lambda)}(\Sigma, \Xi)$ operator in terms of basis bras and kets in the

S and I subspaces as follows

$$\begin{aligned}
Q^{(\Lambda,\lambda)}(\Sigma, \Xi) &= (-1)^{\Sigma-\Xi} ([\Lambda][\Sigma][\Xi])^{1/2} \sum (-1)^{S+I-n-m} \\
&\begin{pmatrix} \Sigma & \Xi & \Lambda \\ p & \rho & -\lambda \end{pmatrix} \begin{pmatrix} S & S & \Sigma \\ \nu & -n & -p \end{pmatrix} \begin{pmatrix} I & I & \Xi \\ \mu & -m & -\rho \end{pmatrix} \\
&|S, \nu\rangle \langle S, n| \otimes |I, \mu\rangle \langle I, m|
\end{aligned} \tag{8}$$

These operators satisfy the following orthonormal criterion

$$Tr \left\{ \left(Q^{(\Lambda',\lambda')}(\Sigma', \Xi') \right)^\dagger Q^{(\Lambda,\lambda)}(\Sigma, \Xi) \right\} = \delta_{\Lambda',\Lambda} \delta_{\lambda',\lambda} \delta_{\Sigma',\Sigma} \delta_{\Xi',\Xi}, \tag{9}$$

as may be shown using the identities in the appendix. Note that the sum in Equation 9 is over all azimuthal quantum numbers, *i.e.* the quantities in the bottom row of the 3j symbols. This will be true for all sums evaluated in the work presented here, unless specifically stated otherwise.

The stochastic Liouville equation [10, 11, 12] allows one to compute the time-dependent response of a spin system to stochastic perturbations in the presence of a relaxation mechanism, *e.g.*, rotational diffusion. Following Blum [6], one may expand the density matrix in terms of the Q operators. The spin-dependent part of the dynamics may then be represented schematically by a relation of the form [5]

$$[Q_1, Q_2] = C_{1,2}^3 Q_3, \tag{10}$$

where $C_{1,2}^3$ may be thought of as a structure constant for the group describing the dynamics, usually $SU(n)$. One may use the Frobenius trace metric to reduce Equation 10 to an evaluation of the structure constants $\{C_{1,2}^3\}$ as follows

$$Tr \left\{ (Q_3)^\dagger [Q_1, Q_2] \right\} = C_{1,2}^3 \tag{11}$$

From this perspective, the spin dynamics are determined by the structure constants $\{C_{1,2}^3\}$, which may be thought of as a generalized form of the Wigner-Eckart Theorem. [5, 6, 7] The power of the Stochastic Liouville Equation method consists of the observation that stochastic perturbations relaxed by rotational diffusion affect the spin dynamics as well as the ‘free’ precession terms characterized by Equation 11.

The advantage of the Q operator formalism is that it emphasizes the group properties of the spin dynamics which may be analyzed independently of the particular model of relaxation. In a sense, $\{Q\}$ is the ‘optimum’ representation for identifying symmetries of the spin dynamics. For example, in theoretical treatments of the saturated lineshape [12, 13] one notes that the operator equivalent of $Q^{(0,0)}$ is decoupled from the dynamics as the observable corresponding to $Q^{(0,0)}$ expresses conservation of probability. However, in systems where populations must be generated, as in photo-excited triplets, the $Q^{(0,0)}$ operator will play an important role in a consistent description of the dynamics. The Q operator formalism allows one to keep track of all these connections in a concise and consistent way. Furthermore, when non-secular terms are unimportant, which is often the case in high field, high frequency EPR, the dynamics are well

described by the *decoupled* evolution of the $Q^{(1,1)}(S)$ and $Q^{(1,-1)}(S)$ operators. These observations can significantly reduce the computational burden required for accurate lineshape calculation, as has been amply documented elsewhere. [1, 10]

Equation 11 may be rewritten in a form that more explicitly demonstrates the close connection to the Wigner-Eckart theorem, as shown by Benetis [7]

$$\begin{aligned} Tr \left\{ \left(Q^{(\Lambda'',\lambda'')}(\Sigma'', \Xi'') \right)^\dagger [Q^{(\Lambda',\lambda')}(\Sigma', \Xi'), Q^{(\Lambda,\lambda)}(\Sigma, \Xi)] \right\} = \\ (-1)^{\Lambda-\Lambda'+\lambda''} [\Lambda'']^{1/2} R_{\Lambda''\Lambda'\Lambda}^{SI}(\Sigma'', \Xi''; \Sigma', \Xi'; \Sigma, \Xi). \end{aligned} \quad (12)$$

Here $R_{\Lambda''\Lambda'\Lambda}^{SI}(\Sigma'', \Xi''; \Sigma', \Xi'; \Sigma, \Xi)$ is a reduced matrix element. Evaluation of the right hand side of Equation 12 gives the structure constants for the group describing the coupled spin space. Computation of the reduced matrix element requires the evaluation of a sum over all azimuthal quantum numbers of the product of 9 Wigner 3j symbols modulated by an azimuthal quantum number dependent phase. Using the identities given in the appendix, it is possible to rewrite the product of six of the 3j symbols into a product of two 3j symbols and two 6j symbols, absorbing the azimuthal phase factor into the definitions of the 6j symbols in the process. The remaining sum over the product of five 3j symbols may then be rewritten in terms of the product of a 3j symbol and a 9j symbol. Keeping track of all the phase factors, Benetis has shown [7]

$$\begin{aligned} R_{\Lambda''\Lambda'\Lambda}^{SI}(\Sigma'', \Xi''; \Sigma', \Xi'; \Sigma, \Xi) = \\ (-1)^{\Lambda'+\Lambda} \left[1 - (-1)^{\Sigma''+\Sigma'+\Sigma+\Xi''+\Xi'+\Xi} \right] (-1)^{\Lambda''+\Sigma''+\Xi''} (-1)^{2S+2I} \\ ([\Lambda'][\Lambda][\Sigma''][\Sigma'][\Sigma][\Xi''][\Xi'][\Xi])^{1/2} \\ \left\{ \begin{array}{ccc} \Sigma'' & \Sigma' & \Sigma \\ S & S & S \end{array} \right\} \left\{ \begin{array}{ccc} \Xi'' & \Xi' & \Xi \\ I & I & I \end{array} \right\} \left\{ \begin{array}{ccc} \Lambda'' & \Lambda' & \Lambda \\ \Sigma'' & \Sigma' & \Sigma \\ \Xi'' & \Xi' & \Xi \end{array} \right\} \end{aligned} \quad (13)$$

Note that the reduced matrix element vanishes unless $\Sigma'' + \Sigma' + \Sigma + \Xi'' + \Xi' + \Xi$ is an odd integer. This imposes constraints on the mechanisms by which particular transitions may be coupled to the dynamics. The advantage of the top-down approach is that such symmetries may simply be read off of the reduced matrix element. Further symmetries follow from the properties of the 3j, 6j and 9j symbols. See the appendix for properties of 3nj symbols that are particularly useful for the manipulations required here.

4 Four Coupled Spins

Distance determinations in spin-labeled macromolecules can yield important insights into structure, which in turn inform models of function. Due to the large magnetic moments of nitroxide spin labels, distance measurements *via* double quantum coherence (DQC) EPR can probe intramolecular distances from 1 to 8

nm. [14] When DQC is infeasible, distance determinations may still be made using alternative experimental techniques such as DEER or PELDOR. [15] When nitroxide spin labels are used, dipolar coupling of the two relevant electrons in addition to the coupling of the nitrogen nuclei to the individual electrons (and in principle to each other), yields a system of four coupled spins. The spin operator method is particularly useful for this case. The appropriate generalization of the two spin Q operators to this case is

$$\begin{aligned}
Q^{(K_i, \kappa_i)}(\Lambda_i, \Sigma_i, \Xi_i, S_1, I_1; \Lambda'_i, \Sigma'_i, \Xi'_i, S_2, I_2) = & \\
(-1)^{\phi_i + S_1 + S_2 + I_1 + I_2} ([K_i][\Lambda_i][\Sigma_i][\Xi_i][\Lambda'_i][\Sigma'_i][\Xi'_i])^{1/2} & \\
\sum (-1)^{\varphi_i} \begin{pmatrix} \Lambda_i & \Lambda'_i & K_i \\ p_i & p'_i & -\kappa_i \end{pmatrix} \begin{pmatrix} \Sigma_i & \Xi_i & \Lambda_i \\ \pi_i & \pi''_i & -p_i \end{pmatrix} & \\
\begin{pmatrix} S_1 & S_1 & \Sigma_i \\ n_i & -n''_i & -\pi_i \end{pmatrix} \begin{pmatrix} I_1 & I_1 & \Xi_i \\ m_i & -m''_i & -\pi''_i \end{pmatrix} \begin{pmatrix} \Sigma'_i & \Xi'_i & \Lambda'_i \\ \pi'_i & \pi'''_i & -p'_i \end{pmatrix} & \quad (14) \\
\begin{pmatrix} S_2 & S_2 & \Sigma'_i \\ n'_i & -n'''_i & -\pi'_i \end{pmatrix} \begin{pmatrix} I_2 & I_2 & \Xi_2 \\ m'_i & -m'''_i & -\pi'''_i \end{pmatrix} & \\
|S_1, n_i\rangle \langle S_1, n''_i| \otimes |I_1, m_i\rangle \langle I_1, m''_i| \otimes |S_2, n'_i\rangle \langle S_2, n'''_i| \otimes |I_2, m'_i\rangle \langle I_2, m'''_i| &
\end{aligned}$$

The phases in Equation 14 are defined as follows

$$\phi_i = \Lambda_i - \Lambda'_i + \Sigma_i - \Xi_i + \Sigma'_i - \Xi'_i \quad (15)$$

and

$$\varphi_i = \kappa_i + p_i + 2\pi_i + 2\pi''_i + p'_i + 2\pi'_i + 2\pi'''_i - n_i - m_i - n'_i - m'_i \quad (16)$$

In order to simplify the notation somewhat, note that unprimed upper case letters will refer to S_1 and I_1 , thus Λ_i will be used as a mnemonic shorthand for $\{\Lambda_i, \Sigma_i, \Xi_i, S_1, I_1\}$. Similarly, Λ'_i is a mnemonic shorthand for $\{\Lambda'_i, \Sigma'_i, \Xi'_i, S_2, I_2\}$. This notation was chosen to facilitate disambiguation of the required spin index. Other choices are possible. With this notation, the left hand side of Equation 14 may be written as $Q^{(K_i, \kappa_i)}(\Lambda_i, \Lambda'_i)$.

These four spin operators satisfy the following orthonormalization condition using the Frobenius trace metric

$$Tr \left\{ \left(Q^{(K_1, \kappa_1)}(\Lambda_1, \Lambda'_1) \right)^\dagger Q^{(K_2, \kappa_2)}(\Lambda_2, \Lambda'_2) \right\} = \delta_{K_1, K_2} \delta_{\kappa_1, \kappa_2} \delta_{\Lambda_1, \Lambda_2} \delta_{\Lambda'_1, \Lambda'_2} \quad (17)$$

With the conventions given above, the notation implies the following additional Kronecker δ functions

$$\delta_{\Lambda_1, \Lambda_2} \rightarrow \delta_{\Lambda_1, \Lambda_2} \delta_{\Sigma_1, \Sigma_2} \delta_{\Xi_1, \Xi_2} \quad (18)$$

and similarly for the primed indices. The four spin operators also satisfy a trace relation for the product of three $Q^{(K, \kappa)}$ operators. This is the spin space analog of the integral relation for the product of three

Wigner rotation matrices

$$\int d\Omega \mathcal{D}_{M_1, K_1}^{L_1}(\Omega) \mathcal{D}_{M_2, K_2}^{L_2}(\Omega) \mathcal{D}_{M_3, K_3}^{L_3}(\Omega) = 8\pi^2 \begin{pmatrix} L_1 & L_2 & L_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L_3 \\ K_1 & K_2 & K_3 \end{pmatrix} \quad (19)$$

One finds

$$\begin{aligned} Tr \left\{ \left(Q^{(K_1, \kappa_1)}(\Lambda_1, \Lambda'_1) \right)^\dagger Q^{(K_2, \kappa_2)}(\Lambda_2, \Lambda'_2) Q^{(K_3, \kappa_3)}(\Lambda_3, \Lambda'_3) \right\} = \\ (-1)^{\Phi + \kappa_1} ([K_1][\Lambda_1][\Sigma_1][\Xi_1][\Lambda'_1][\Sigma'_1][\Xi'_1][K_2][\Lambda_2][\Sigma_2][\Xi_2][\Lambda'_2][\Sigma'_2][\Xi'_2][K_3][\Lambda_3][\Sigma_3][\Xi_3][\Lambda'_3][\Sigma'_3][\Xi'_3])^{1/2} \\ \begin{pmatrix} K_3 & K_2 & K_1 \\ \kappa_3 & \kappa_2 & -\kappa_1 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & K_3 \\ \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \end{pmatrix} \begin{pmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Sigma_1 & \Sigma_2 & \Sigma_3 \\ \Xi_1 & \Xi_2 & \Xi_3 \end{pmatrix} \begin{pmatrix} \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \\ \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ \Xi'_1 & \Xi'_2 & \Xi'_3 \end{pmatrix} \\ \begin{pmatrix} \Sigma_1 & \Sigma_2 & \Sigma_3 \\ S_1 & S_1 & S_1 \end{pmatrix} \begin{pmatrix} \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ S_2 & S_2 & S_2 \end{pmatrix} \begin{pmatrix} \Xi_1 & \Xi_2 & \Xi_3 \\ I_1 & I_1 & I_1 \end{pmatrix} \begin{pmatrix} \Xi'_1 & \Xi'_2 & \Xi'_3 \\ I_2 & I_2 & I_2 \end{pmatrix}, \end{aligned} \quad (20)$$

where

$$\Phi = K_1 + \Sigma_1 + \Xi_1 + \Sigma'_1 + \Xi'_1 + 2S_1 + 2S_2 + 2I_1 + 2I_2 \quad (21)$$

Using the symmetries of the 3j, 6j and 9j symbols given in the appendix, one can construct the structure constant, or equivalently, the reduced matrix element for the coupled four spin case

$$\begin{aligned} Tr \left\{ \left(Q^{(K_1, \kappa_1)}(\Lambda_1, \Lambda'_1) \right)^\dagger \left[Q^{(K_2, \kappa_2)}(\Lambda_2, \Lambda'_2), Q^{(K_3, \kappa_3)}(\Lambda_3, \Lambda'_3) \right] \right\} = \\ (-1)^{\Phi + \kappa_1} [K_1]^{1/2} [W]^{1/2} \left[1 - (-1)^{\Sigma_1 + \Sigma_2 + \Sigma_3 + \Xi_1 + \Xi_2 + \Xi_3 + \Sigma'_1 + \Sigma'_2 + \Sigma'_3 + \Xi'_1 + \Xi'_2 + \Xi'_3} \right] \\ \begin{pmatrix} K_3 & K_2 & K_1 \\ \kappa_3 & \kappa_2 & -\kappa_1 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & K_3 \\ \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \end{pmatrix} \begin{pmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Sigma_1 & \Sigma_2 & \Sigma_3 \\ \Xi_1 & \Xi_2 & \Xi_3 \end{pmatrix} \begin{pmatrix} \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \\ \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ \Xi'_1 & \Xi'_2 & \Xi'_3 \end{pmatrix} \\ \begin{pmatrix} \Sigma_1 & \Sigma_2 & \Sigma_3 \\ S_1 & S_1 & S_1 \end{pmatrix} \begin{pmatrix} \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ S_2 & S_2 & S_2 \end{pmatrix} \begin{pmatrix} \Xi_1 & \Xi_2 & \Xi_3 \\ I_1 & I_1 & I_1 \end{pmatrix} \begin{pmatrix} \Xi'_1 & \Xi'_2 & \Xi'_3 \\ I_2 & I_2 & I_2 \end{pmatrix}, \end{aligned} \quad (22)$$

where

$$[W] \equiv [\Lambda_1][\Sigma_1][\Xi_1][\Lambda'_1][\Sigma'_1][\Xi'_1][K_2][\Lambda_2][\Sigma_2][\Xi_2][\Lambda'_2][\Sigma'_2][\Xi'_2][K_3][\Lambda_3][\Sigma_3][\Xi_3][\Lambda'_3][\Sigma'_3][\Xi'_3] \quad (23)$$

Note that the structure constant vanishes unless the sum of the Σ , Σ' , Ξ and Ξ' indices is odd. This is the analog of the structure constant condition derived for the two coupled spin case.

One may now rewrite this Equation 22 in a form that displays more clearly its relationship to the

Wigner-Eckart theorem

$$Tr \left\{ \left(Q^{(K_1, \kappa_1)}(\Lambda_1, \Lambda'_1) \right)^\dagger \left[Q^{(K_2, \kappa_2)}(\Lambda_2, \Lambda'_2), Q^{(K_3, \kappa_3)}(\Lambda_3, \Lambda'_3) \right] \right\} = \quad (24)$$

$$(-1)^{K_3 - K_2 + \kappa_1} [K_1]^{1/2} \begin{pmatrix} K_3 & K_2 & K_1 \\ \kappa_3 & \kappa_2 & -\kappa_1 \end{pmatrix} R_{K_1 K_2 K_3}^{S_1 S_2 I_1 I_2}(\Lambda_1, \Lambda'_1; \Lambda_2, \Lambda'_2; \Lambda_3, \Lambda'_3),$$

where

$$R_{K_1 K_2 K_3}^{S_1 S_2 I_1 I_2}(\Lambda_1, \Lambda'_1; \Lambda_2, \Lambda'_2; \Lambda_3, \Lambda'_3) = \quad (25)$$

$$(-1)^{K_3 + K_2} [W]^{1/2} (-1)^{K_1 + \Sigma_1 + \Xi_1 + \Sigma'_1 + \Xi'_1} (-1)^{2S_1 + 2S_2 + 2I_1 + 2I_2}$$

$$\left[1 - (-1)^{\Sigma_1 + \Sigma_2 + \Sigma_3 + \Xi_1 + \Xi_2 + \Xi_3 + \Sigma'_1 + \Sigma'_2 + \Sigma'_3 + \Xi'_1 + \Xi'_2 + \Xi'_3} \right]$$

$$\begin{Bmatrix} \Sigma_1 & \Sigma_2 & \Sigma_3 \\ S_1 & S_1 & S_1 \end{Bmatrix} \begin{Bmatrix} \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ S_2 & S_2 & S_2 \end{Bmatrix} \begin{Bmatrix} \Xi_1 & \Xi_2 & \Xi_3 \\ I_1 & I_1 & I_1 \end{Bmatrix} \begin{Bmatrix} \Xi'_1 & \Xi'_2 & \Xi'_3 \\ I_2 & I_2 & I_2 \end{Bmatrix}$$

$$\begin{Bmatrix} K_1 & K_2 & K_3 \\ \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \end{Bmatrix} \begin{Bmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Sigma_1 & \Sigma_2 & \Sigma_3 \\ \Xi_1 & \Xi_2 & \Xi_3 \end{Bmatrix} \begin{Bmatrix} \Lambda'_1 & \Lambda'_2 & \Lambda'_3 \\ \Sigma'_1 & \Sigma'_2 & \Sigma'_3 \\ \Xi'_1 & \Xi'_2 & \Xi'_3 \end{Bmatrix}$$

When $I_2 = S_2 = 0$ all of the primed indices vanish. The properties of the 6j and 9j symbols given in the appendix allow one to show that Equation 25 reduces to Equation 13 where the degenerate 9j symbol with three vanishing arguments gives

$$\begin{Bmatrix} K_1 & K_2 & K_3 \\ \Lambda_1 & \Lambda_2 & \Lambda_3 \\ 0 & 0 & 0 \end{Bmatrix} = \frac{\delta_{K_1, \Lambda_1} \delta_{K_2, \Lambda_2} \delta_{K_3, \Lambda_3}}{([\Lambda_1][\Lambda_2][\Lambda_3])^{1/2}} \quad (26)$$

Wigner 3j, 6j and 9j symbols with all zero entries are equal to one. Thus, the case of a single S spin coupled to a single I spin is a special case of the four spin formalism developed here. For the case of one uncoupled spin, where the only non-zero spin is, say, S_1 , the Wigner-Eckart theorem states

$$Tr \left\{ \left(Q^{(\Sigma_1, \sigma_1)} \right)^\dagger \left[Q^{(\Sigma_2, \sigma_2)}, Q^{(\Sigma_3, \sigma_3)} \right] \right\} = (-1)^{\Sigma_3 - \Sigma_2 + \sigma_1} [\Sigma_1]^{1/2} \begin{pmatrix} \Sigma_3 & \Sigma_2 & \Sigma_1 \\ \sigma_3 & \sigma_2 & -\sigma_3 \end{pmatrix} R_{\Sigma_1 \Sigma_2 \Sigma_3}^{S_1}, \quad (27)$$

where

$$R_{\Sigma_1 \Sigma_2 \Sigma_3}^{S_1} = (-1)^{\Sigma_3 + \Sigma_2} ([\Sigma_2][\Sigma_3])^{1/2} \begin{Bmatrix} \Sigma_3 & \Sigma_2 & \Sigma_1 \\ S_1 & S_1 & S_1 \end{Bmatrix} [1 - (-1)^{\Sigma_1 + \Sigma_2 + \Sigma_3}] \quad (28)$$

5 Summary

The expressions developed here for the reduced matrix elements may be applied to a variety of situations. The reduced matrix elements for one spin operator may be used to write the Liouville operator matrix

elements for the Zeeman interaction. The two spin operators may be used to compute the Liouville operator matrix elements for the hyperfine interaction between an S and an I spin, or the dipolar interaction between two S or two I spins. At low fields, where the coupled representation is preferred on physical grounds, the current formalism may be used to write the appropriate matrix elements for four strongly coupled spins treated as a single spin as well. [17]

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A Useful 3nj identities

In deriving identities for 3nj symbols, the following orthogonality relation is particularly useful [16]

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{\delta_{j_3, j'_3} \delta_{m_3, m'_3}}{[j_2]} \quad (29)$$

One may use this result to write down the following completeness relation

$$\sum_{m_1, m_2, m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}^2 = 1 \quad (30)$$

In the sum over products of 3j symbols that occur in this work, it is often the case that three of the 3j symbols share a common set of angular momentum indices. The definition of the 6j symbol depends on the sum over the azimuthal quantum numbers of a product of four 3j symbols:

$$\frac{\delta_{j_3, j'_3} \delta_{m_3, m'_3}}{[j_3]} \begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} = \sum_{M_1, M_2, M_3, m_1, m_2} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} \begin{pmatrix} J_2 & J_3 & j_1 \\ M_2 & -M_3 & m_1 \end{pmatrix} \begin{pmatrix} J_3 & J_1 & j_2 \\ M_3 & -M_1 & m_2 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & -M_2 & m_3 \end{pmatrix} \quad (31)$$

Note that the left hand side of Equation 31 may be rewritten by expressing the prefactor in terms of Equation 29:

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{matrix} \right\} = \quad (32)$$

$$\sum_{M_1, M_2, M_3, m_1, m_2} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3}$$

$$\begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} \begin{pmatrix} J_2 & J_3 & j_1 \\ M_2 & -M_3 & m_1 \end{pmatrix} \begin{pmatrix} J_3 & J_1 & j_2 \\ M_3 & -M_1 & m_2 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & -M_2 & m_3 \end{pmatrix}$$

Given that both sums in Equation 32 converge, one may identify terms on both sides of Equation 32 that share a common factor, in this case, the 3j symbol depending on j'_3 . This allows one to write

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{matrix} \right\} = \quad (33)$$

$$\sum_{M_1, M_2, M_3} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3}$$

$$\begin{pmatrix} J_2 & J_3 & j_1 \\ M_2 & -M_3 & m_1 \end{pmatrix} \begin{pmatrix} J_3 & J_1 & j_2 \\ M_3 & -M_1 & m_2 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & -M_2 & m_3 \end{pmatrix}$$

Note that the equivalent expression in Brink and Satchler [16] has a misprint: the 6j symbol given here is printed in that work as a 3j symbol. This is the only error that this author has ever found in Brink and Satchler.

One also finds in the calculations reported here that there are products of five 3j symbols with a common set of magnetic quantum numbers. The 9j symbol may be defined as the following contraction of six 3j symbols:

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{matrix} \right\} = \quad (34)$$

$$\sum \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_6 \\ m_4 & m_5 & m_6 \end{pmatrix} \begin{pmatrix} j_7 & j_8 & j_9 \\ m_7 & m_8 & m_9 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_4 & j_7 \\ m_1 & m_4 & m_7 \end{pmatrix} \begin{pmatrix} j_2 & j_5 & j_8 \\ m_2 & m_5 & m_8 \end{pmatrix} \begin{pmatrix} j_3 & j_6 & j_9 \\ m_3 & m_6 & m_9 \end{pmatrix}.$$

Note that in Equation 34 the sum is over all azimuthal quantum numbers, according to the convention for sums used here. Note also that unlike the case of the 6j symbols, there are no phases appearing in the sum. When using 9j symbols in the calculations reported here, it is important to verify that all of the remaining *azimuthal* quantum numbers in the phases that appear in the trace sum to an even integer and therefore drop out of the problem. This follows from repeated application of the observation that the azimuthal

quantum numbers in a 3j symbol sum to zero and the observation that the Kronecker delta functions that appear in the trace over spin states enforce constraints on the allowed values of the azimuthal quantum numbers. This point will be addressed more fully below.

In order to rewrite the 9j identity in terms of a product of five 3j symbols, premultiply Equation 34 by the left hand side of Equation 30. One finds

$$\begin{aligned} \sum_{m_1, m_2, m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}^2 \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{matrix} \right\} = & \quad (35) \\ \sum \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_6 \\ m_4 & m_5 & m_6 \end{pmatrix} \begin{pmatrix} j_7 & j_8 & j_9 \\ m_7 & m_8 & m_9 \end{pmatrix} \\ \begin{pmatrix} j_1 & j_4 & j_7 \\ m_1 & m_4 & m_7 \end{pmatrix} \begin{pmatrix} j_2 & j_5 & j_8 \\ m_2 & m_5 & m_8 \end{pmatrix} \begin{pmatrix} j_3 & j_6 & j_9 \\ m_3 & m_6 & m_9 \end{pmatrix}. \end{aligned}$$

Note that since both sums converge, one may use the same trick of identifying common terms on both sides of Equation 35 that was used to derive the identity for the product of a 3j and 6j symbol. One finds

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{matrix} \right\} = & \quad (36) \\ \sum_{m_4, m_5, m_6, m_7, m_8, m_9} \begin{pmatrix} j_4 & j_5 & j_6 \\ m_4 & m_5 & m_6 \end{pmatrix} \begin{pmatrix} j_7 & j_8 & j_9 \\ m_7 & m_8 & m_9 \end{pmatrix} \\ \begin{pmatrix} j_1 & j_4 & j_7 \\ m_1 & m_4 & m_7 \end{pmatrix} \begin{pmatrix} j_2 & j_5 & j_8 \\ m_2 & m_5 & m_8 \end{pmatrix} \begin{pmatrix} j_3 & j_6 & j_9 \\ m_3 & m_6 & m_9 \end{pmatrix}. \end{aligned}$$

Repeated application of the identities Equation 33 and Equation 36 allow one to collapse the sum over azimuthal quantum numbers of the product of twenty-one 3j symbols that occur in the trace over three Q operators into a product of one 3j symbol, three 9j symbols and four 6j symbols. As an added benefit, the sums over azimuthal quantum numbers appear only implicitly in the definitions of the 6j and 9j symbols, leading to expressions that are less cluttered than the equivalent expressions in the uncoupled basis, although, admittedly, clutter is often in the eye of the beholder.

A.1 Manipulations of 3nj symbols

The 3j symbols have a number of important and useful symmetries. The most important ones for the current application are the following:

- Changing the sign of *all* azimuthal quantum numbers in a 3j symbol multiplies the 3j symbol by a phase factor $(-1)^{j_1+j_2+j_3}$.

- an even permutation of the columns of a 3j symbol leaves the 3j symbol unaffected.
- an odd permutation of the columns of a 3j symbol multiplies the 3j symbol by a phase factor $(-1)^{j_1+j_2+j_3}$.
- the sum $j_1 + j_2 + j_3$ is an integer
- the sum $m_1 + m_2 + m_3 = 0$.

The following properties of 6j symbols are useful in the derivations reported here

- The 6j symbols are unaffected by odd or even permutations of columns.
- The 6j symbols are unaffected by an interchange of the upper and lower entries in any two columns

The following properties of 9j symbols are useful in the derivations reported here

- The 9j symbols are unaffected by an interchange of rows and columns (reflection about a diagonal)
- interchange of adjacent rows or columns multiplies the 9j symbol by a phase factor $(-1)^{\sum j_i}$

In computing the structure constant associated with $Tr \{(Q_1)^\dagger [Q_2, Q_3]\}$ it is useful to have an expression in terms of $Tr \{(Q_1)^\dagger Q_2 Q_3\}$ and $Tr \{(Q_1)^\dagger Q_3 Q_2\}$. From the structure of the reduced matrix element the latter expression can be derived from the former by interchanging the second and third columns of every 3nj symbol, which is an odd permutation. From the properties given above, the 6j symbols are unaffected by interchange of the second and third columns. The relevant arguments of the 3j and 9j symbols are all integers, so the phase factor resulting from interchange will have a contribution differing from unity only for those arguments that occur an odd number of times in the 3j and 9j symbols.

In reshaping products of three 3j symbols to put them into the form of Equation 33 it is useful to note that the substitution $m \rightarrow -m$ over dummy indices allows one to obtain the correct phase factor. Once this has been done it is often necessary to change the signs of all the azimuthal quantum numbers in one or more 3j symbols in order to have the arguments correspond to the definition given in Equation 33. The relevant 3j symbol is then multiplied by the appropriate phase factor according to the rules given above. These considerations are also valid for the manipulations required to put products of five 3j symbols into the form of Equation 36. Although the approach given here is an algebraic one, equivalent results may be derived by graphical methods. [9, 16, 18]

A.2 Constraints on Azimuthal Quantum Numbers

In the computation of the structure constant, traces of the following form arise

$$Tr_{S_1} \{|S_1, n_1''\rangle \langle S_1, n_1| S_1, n_2\rangle \langle S_1, n_2''| S_1, n_3\rangle \langle S_1, n_3''|\} = \delta_{n_1'', n_3''} \delta_{n_1, n_2} \delta_{n_2'', n_3} \quad (37)$$

Note that the order of the first ket-bra is due to the adjoint operation in the definition of the Frobenius trace metric. Given that the phases of all the terms have been carefully orchestrated to render the coefficients of $\{Q\}$ real, the adjoint operation merely transposes the relevant bra and ket. After evaluation of the traces one finds the following Kronecker delta functions, which may be used to manipulate the sum over the product of twenty-one $3j$ symbols along the lines indicated above:

$$Tr \rightarrow \delta_{n'_1, n'_3} \delta_{n_1, n_2} \delta_{n'_2, n_3} \delta_{n''_1, n''_3} \delta_{n'_1, n'_2} \delta_{n''_2, n'_3} \delta_{m'_1, m'_3} \delta_{m_1, m_2} \delta_{m'_2, m_3} \delta_{m''_1, m''_3} \delta_{m'_1, m'_2} \delta_{m''_2, m'_3} \quad (38)$$

A.3 Degenerate $3nj$ symbols

The following identities are useful for reducing the structure constant to a simpler form when a relevant angular momentum vanishes. The structure constant(s) for 1 or 2–4 coupled spins are all then derivable as special cases of Equation 25

A.3.1 $3j$ symbol identities [16]

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & m_2 & 0 \end{pmatrix} = (-1)^{j_1 - m_1} \frac{\delta_{j_1, j_2} \delta_{m_1, -m_2}}{[j_1]^{1/2}} \quad (39)$$

Furthermore

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = 1 \quad (40)$$

A.3.2 $6j$ symbol identities [9]

$$\left\{ \begin{matrix} j_1 & j_2 & 0 \\ j_4 & j_5 & j_6 \end{matrix} \right\} = (-1)^{j_1 + j_4 + j_6} \frac{\delta_{j_1, j_2} \delta_{j_4, j_5}}{([j_1][j_4])^{1/2}} \quad (41)$$

Note that

$$\left\{ \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \right\} = 1 \quad (42)$$

A.3.3 $9j$ symbol identities [9]

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & 0 \end{matrix} \right\} = (-1)^{j_2 + j_3 + j_4 + j_7} \frac{\delta_{j_3, j_6} \delta_{j_7, j_8}}{([j_3][j_7])^{1/2}} \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_5 & j_4 & j_7 \end{matrix} \right\} \quad (43)$$

When $j_7 = 0$, Equation 43 simplifies further. Note that the Kronecker δ function in Equation 43 enforces the condition $j_7 = j_8$. One finds

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ 0 & 0 & 0 \end{matrix} \right\} = (-1)^{j_2 + j_3 + j_4} \frac{\delta_{j_3, j_6}}{[j_3]^{1/2}} \left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_5 & j_4 & 0 \end{matrix} \right\} \quad (44)$$

At this point, one can interchange the arguments in the top and bottom rows of the second and third columns of the 6j symbol in Equation 44 in order to put it in the form of Equation 41. Keeping track of the phases and the order of arguments in the 6j symbol in Equation 44 one finds

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ 0 & 0 & 0 \end{array} \right\} = \frac{\delta_{j_1, j_4} \delta_{j_2, j_5} \delta_{j_3, j_6}}{([j_1][j_2][j_3])^{1/2}} \quad (45)$$

Zare [9] notes that triangle conditions on the arguments of the 6j symbol enforce the condition that $2(j_1 + j_2 + j_3)$ is an even integer. This allows one to omit a phase factor that would otherwise premultiply Equation 45. When $j_1 = j_2 = j_3 = 0$ the 9j symbol has all zero entries on account of the Kronecker δ functions in Equation 45. In that case, one finds

$$\left\{ \begin{array}{ccc} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array} \right\} = 1 \quad (46)$$