

A Complete Hermitian Operator Basis Set for any Spin Quantum Number

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A new Hermitian operator basis set for spins of any quantum number is presented for use in simulations of NMR experiments. The advantage with a Hermitian operator basis is that the Liouville–von Neumann equation, including relaxation with dynamic frequency shifts, is real. Real algebra makes numerical calculations faster and simplifies physical interpretation of the equation system as compared to complex algebra. The unity operator is included in the Hermitian operator basis, which makes it easy to rewrite the inhomogeneous Liouville–von Neumann equation into a homogeneous form. The unity operator also simplifies physical interpretation of the equation system for coupled spin systems. © 2001 Academic Press

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INTRODUCTION

Rapid simulation of NMR experiments is important in the development and optimization of pulse sequences, mixing sequences, shaped pulses, and other tools in the toolbox of modern NMR. Simulations have also shown to be useful in the analysis of experimental results concerning structures and dynamics of molecules. This paper describes a way to make simulations of NMR experiments involving spins with a quantum number larger than $\frac{1}{2}$ faster than using other methods.

Calculations of the spin dynamics involving spin $S > \frac{1}{2}$ nuclei have traditionally been performed using an operator basis consisting of either the level shift operators (1) or the irreducible tensor operators (2). There exists also other useful operator basis sets such as Cartesian product operators (3, 4), products of shift operators (5), polarization operators (6), and the Cartesian single-transition operators (7, 8).

Here we present a new complete operator basis set for any spin quantum number. The operator basis is Hermitian and it includes the unity operator. The basis set is constructed from linear combinations of the irreducible tensor operators.

The Liouville–von Neumann equation, the quantum mechanical master equation, is real when expressed in a Hermitian basis (9). A physical observable is described by a real value and a

Hermitian operator does have a real eigenvalue. A quantum mechanical operator corresponding to a physical observable is thus always Hermitian (10). A Hermitian operator basis simplifies physical interpretation of the quantum mechanical master equation and makes numerical calculations faster because it uses only real algebra. The master equation is real even when relaxation, with or without dynamic frequency shifts (11), is included. There are also several advantages with having the unity operator in the set of basis operators. It is then easy to rewrite the Liouville–von Neumann equation including relaxation, into a homogeneous form from its usual inhomogeneous form (12, 13). The physical interpretation of the Liouville–von Neumann equation for coupled spin systems also becomes easier when the unity operator is included because the respective single-spin operators are then a part of the complete set of basis operators.

THEORY

We will first discuss the development of the new set of Hermitian basis operators. We will then use this basis to set up the Liouville–von Neumann equation including both coherent and incoherent (relaxation) contributions for both a spin $S = 1$ nucleus and a spin $S = \frac{3}{2}$ nucleus. The Liouville–von Neumann equation is finally rewritten into a mathematically homogeneous form from its usual inhomogeneous form.

Hermitian Operator Basis

The basis to be presented is based on linear combinations of irreducible tensor operators. The matrix representations of the irreducible tensor operators can be calculated using Wigner 3-J symbols, according to (2)

$$T_{k,q}^S = \sqrt{2S+1}\sqrt{2k+1} \sum_{M=-S}^S \sum_{Mp=-S}^S (-1)^{(S-M)} \times \begin{bmatrix} S & k & S \\ -M & q & Mp \end{bmatrix} |S, M\rangle \langle S, Mp|, \quad [1]$$

where $0 \leq k \leq 2S$ and $-k \leq q \leq k$ in steps of 1. The normalization is such that $T_{0,0}^S = E$ for any spin quantum number S . It is well known that the Cartesian product operators S_x , S_y , and

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S_z for a spin $S = \frac{1}{2}$ nucleus are Hermitian and can be calculated from irreducible tensor operators according to (5)

$$S_x = \frac{1}{2\sqrt{2}}(T_{1,-1}^{\frac{1}{2}} - T_{1,1}^{\frac{1}{2}}), \quad [2]$$

$$S_y = \frac{i}{2\sqrt{2}}(T_{1,-1}^{\frac{1}{2}} + T_{1,1}^{\frac{1}{2}}), \quad [3]$$

$$S_z = \frac{1}{2}T_{1,0}^{\frac{1}{2}}. \quad [4]$$

Inspired by this we form linear combinations of the irreducible tensor operators not only for single-quantum coherences, but for all coherences according to

$$C_{k,qx}^S = \frac{\sqrt{S(S+1)/3}}{\sqrt{2}}(T_{k,-q}^S + (-1)^q T_{k,q}^S) \quad q \neq 0, \quad [5]$$

$$C_{k,qy}^S = \frac{i\sqrt{S(S+1)/3}}{\sqrt{2}}(T_{k,-q}^S - (-1)^q T_{k,q}^S) \quad q \neq 0, \quad [6]$$

$$C_{k,z}^S = \sqrt{S(S+1)/3} T_{k,0}^S \quad q = 0, \quad [7]$$

where $0 \leq k \leq 2S$ and $0 \leq q \leq k$ in steps of 1. It is easy to show that these operators are orthogonal to each other and that they are Hermitian using well-known relations for the irreducible tensor operators. The basis is normalized so that $C_{1,x}^S = S_x$, $C_{1,y}^S = S_y$, and $C_{1,0}^S = S_z$ irrespective of spin quantum number S , i.e.,

$$\langle C_r | C_s \rangle = \text{Tr}\{C_r^{\text{Adj.}} C_s\} = \delta_{r,s} \frac{S(S+1)(2S+1)}{3}, \quad [8]$$

where C_r and C_s are the basis operators and Adj. stands for the adjoint. In the present case we are using a Hermitian basis, which by definition is self-adjoint, $C^{\text{Adj.}} = C$, and the distinction is obviously irrelevant.

Hermitian Basis for Spin $S = 1$

There are a total of $(2S+1)^2 = 9$ orthogonal operators for spin $S = 1$. These are according to Eqs. [1] and [5]–[7]

$$C_{0,z}^1 = \sqrt{2/3}E = \sqrt{2/3} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad [9]$$

$$C_{1,y}^1 = S_y = \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad [10]$$

$$C_{1,z}^1 = S_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad [11]$$

$$C_{1,x}^1 = S_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \quad [12]$$

$$C_{2,2y}^1 = S_x S_y + S_y S_x = i \begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad [13]$$

$$C_{2,y}^1 = S_z S_y + S_y S_z = \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}, \quad [14]$$

$$C_{2,z}^1 = \sqrt{3}(S_z^2 - 2E/3) = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad [15]$$

$$C_{2,x}^1 = S_z S_x + S_x S_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}, \quad [16]$$

$$C_{2,2x}^1 = S_x^2 - S_y^2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}. \quad [17]$$

The operators and thus the matrices are orthogonal to each other and normalized according to Eq. [8]. Several of these operators can be named according to the product operator formalism (3). The operator $C_{2,x}^1 = S_z S_x + S_x S_z$ corresponds to single-quantum antiphase x magnetization while $C_{2,y}^1 = S_z S_y + S_y S_z$ corresponds to single-quantum antiphase y magnetization. The operators $C_{2,2x}^1 = S_x^2 - S_y^2$ and $C_{2,2y}^1 = S_x S_y + S_y S_x$ are denoted double-quantum coherence x and y magnetization, respectively.

Homogeneous Master Equation

The Liouville–von Neumann equation including relaxation can be written using superoperators such as (5)

$$\frac{d}{dt}\sigma = -(i\hat{H} + \hat{\Gamma})\sigma + \hat{\Gamma}\sigma_0, \quad [18]$$

with

$$\hat{H}\sigma = [H, \sigma], \quad [19]$$

where σ is the density operator as a function of time, σ_0 is the density operator at equilibrium, H is the Hamiltonian, \hat{H} is the commutator superoperator of the Hamiltonian, and $\hat{\Gamma}$ is the relaxation superoperator. \hat{H} corresponds to the coherent contribution and $\hat{\Gamma}$ to the incoherent contribution to the master equation. Double carets indicate superoperators.

The Liouville–von Neumann equation can easily be rewritten in a homogeneous form (I) when the unity operator is included in the basis (12, 13)

$$\frac{d}{dt}\sigma = -(i\hat{H} + \hat{\Gamma})\sigma + \hat{\Gamma}\sigma_0 \rightarrow \frac{d}{dt}\sigma = -(i\hat{H} + \hat{\Gamma}_{\text{improved}})\sigma. \quad [20]$$

One method for doing it is to include the vector corresponding to the relaxation superoperator multiplied with the equilibrium density operator, $\hat{\Gamma}\sigma_0$, as the column in the matrix ($i\hat{H} + \hat{\Gamma}$) at the position corresponding to the unity operator, column 1. Both the row and the column corresponding to the unity operator in the density operator are zero before being used to make the inhomogeneous master equation homogeneous, see Eq. [31].

The Coherent Contribution

The isotropic liquid Hamiltonian, H , for spin $S > \frac{1}{2}$ with nuclear quadrupolar coupling and an axially symmetric electric field gradient tensor in the presence of an RF field in the rotating frame is (3, 5)

$$H = \Omega S_z + \omega_Q \left(S_z^2 - \frac{1}{3} S^2 \right) + \omega_x S_x + \omega_y S_y, \quad [21]$$

with

$$\begin{aligned} \Omega &= \omega_0 - \omega_{\text{RF}}, \\ \omega_x &= -\gamma B_1 \cos(\phi), \\ \omega_y &= -\gamma B_1 \sin(\phi), \end{aligned} \quad [22]$$

and

$$\omega_Q = \frac{3e^2qQ}{4S(2S-1)\hbar}, \quad [23]$$

where Ω is the offset chemical shift frequency, ω_Q is the quadrupolar frequency, ω_x and ω_y are the components of the RF field along the x and y axes, respectively, ω_0 is the Larmor frequency, ω_{RF} is the frequency of the RF field, γB_1 is the magnetogyric ratio times the strength of the RF field, ϕ is the phase of the RF field, e is the elementary charge, q is the principal component of the electric field gradient tensor, and Q is the electric quadrupole moment of the nucleus. The quadrupolar frequency ω_Q averages to 0 in isotropic liquid state and should not really be present in the current Hamiltonian. A small fraction of the quadrupolar interaction can however remain in partially oriented systems (14, 15). The Hamiltonian commutation superoperator can be calculated matrix element by element for any set of basis operators B according to (5)

$$\begin{aligned} H_{rs} &= \frac{\langle B_r | \hat{H} | B_s \rangle}{\langle B_r | B_r \rangle} = \frac{\langle B_r | [H, B_s] \rangle}{\langle B_r | B_r \rangle} \\ &= \frac{\langle B_r | HB_s - B_s H \rangle}{\langle B_r | B_r \rangle} = \frac{\text{Tr}\{B_r^{\text{Adj.}}(HB_s - B_s H)\}}{\text{Tr}\{B_r^{\text{Adj.}} B_r\}}. \end{aligned} \quad [24]$$

All these elements are purely imaginary if the operator basis set B is Hermitian, thus making the coherent part of the Liouville-von Neumann equation real (9).

Dynamic Model

The relaxation rates and dynamic frequency shifts are dependent on the dynamics of the nucleus studied (16, 17). A dynamic model can be used to describe the motional properties of vectors in nuclei and molecules. The dynamic model can then be used to calculate an analytical complex spectral density function, $G(\omega)$. The relaxation rates are functions of the real part of the spectral density function, $J(\omega)$, at certain angular frequencies. The most common and simple real spectral density function is the single Lorentzian

$$J(\omega) = \frac{2}{5} \frac{\tau_c}{1 + (\omega\tau_c)^2}, \quad [25]$$

where τ_c is the correlation time. The imaginary contribution to the complex spectral density function, $L(\omega)$, is defined as the Hilbert transform of $J(\omega)$ and can be identified with a dynamic frequency shift (11). The imaginary contribution is (11)

$$L(\omega) = \frac{2}{5} \frac{\omega\tau_c^2}{1 + (\omega\tau_c)^2}. \quad [26]$$

The real part of the spectral density function is an even function of frequency while the imaginary part is an odd function of frequency.

Relaxation

The elements of the Redfield relaxation matrix for quadrupole relaxation including dynamic frequency shifts on the basis of any complete set of operators B can be calculated according to

$$\begin{aligned} \Gamma_{rs} &= \frac{1}{18} \omega_Q^2 \sum_{q=-2}^2 (J(q\omega)) \\ &\quad - iL(q\omega) \text{Tr} \left\{ \frac{[A_{2,q}^S, B_r]^{\text{Adj.}} [A_{2,q}^S, B_s]}{\langle B_r | B_r \rangle} \right\}, \end{aligned} \quad [27]$$

with the interaction operators for quadrupole relaxation (14)

$$\begin{aligned} A_{2,0}^S &= 3S_z^2 - S^2, \\ A_{2,\pm 1}^S &= \mp \frac{\sqrt{6}}{2} (S_z S_{\pm} + S_{\pm} S_z), \\ A_{2,\pm 2}^S &= \frac{\sqrt{6}}{2} S_{\pm}^2, \end{aligned} \quad [28]$$

and the following relations for the odd and even spectral density functions

$$\begin{aligned} J(-\omega) &= J(\omega), \\ L(0) &= 0, \\ L(-\omega) &= -L(\omega), \end{aligned} \quad [29]$$

in which $J(\omega)$ is the real component and $L(\omega)$ is the imaginary component of the complex spectral density function $G(\omega)$. The relaxation rates are calculated assuming an isotropic liquid and an axially symmetric electric field gradient tensor. Relaxation in locally anisotropic systems requires further considerations (14, 15).

The Homogeneous Master Equation for Spin $S = 1$

The coherent part of the master equation calculated using Eq. [24] and Eq. [18] for the particular case of a single isolated spin $S = 1$ nucleus in the Hermitian basis is

$$\frac{d}{dt} \begin{bmatrix} C_{0,z} \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \end{bmatrix} = - \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_x & -\Omega & 0 & 0 & 0 & -\omega_Q & 0 \\ 0 & -\omega_x & 0 & \omega_y & 0 & 0 & 0 & 0 & 0 \\ 0 & \Omega & -\omega_y & 0 & 0 & \omega_Q & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\omega_y & 0 & \omega_x & -2\Omega \\ 0 & 0 & 0 & -\omega_Q & \omega_y & 0 & \sqrt{3}\omega_x & -\Omega & \omega_x \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{3}\omega_x & 0 & \sqrt{3}\omega_y & 0 \\ 0 & \omega_Q & 0 & 0 & -\omega_x & \Omega & -\sqrt{3}\omega_y & 0 & \omega_y \\ 0 & 0 & 0 & 0 & 2\Omega & -\omega_x & 0 & -\omega_y & 0 \end{bmatrix} \begin{bmatrix} C_{0,z} \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \end{bmatrix}, \quad [30]$$

where all parameters have already been defined.

The relaxation superoperator for a spin $S = 1$ nucleus calculated according to Eq. [27] and Eq. [18] is

$$\hat{\Gamma} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \lambda & 0 & -\omega^{\text{dfs}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \rho & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \omega^{\text{dfs}} & 0 & \lambda & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \lambda^{22} & 0 & 0 & -2\omega^{\text{dfs}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \lambda^{21} & 0 & -\omega^{\text{dfs}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \rho^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \omega^{\text{dfs}} & 0 & \lambda^{21} & 0 \\ 0 & 0 & 0 & 0 & 2\omega^{\text{dfs}} & 0 & 0 & 0 & \lambda^{22} \end{bmatrix}, \quad \hat{\Gamma}\sigma_0 = \begin{bmatrix} 0 \\ 0 \\ M_0\rho \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad [31]$$

in which M_0 is the equilibrium magnetization. The relaxation rates are

$$\lambda = \frac{1}{6}\omega_Q^2[3J(0) + 5J(\omega) + 2J(2\omega)], \quad [32]$$

$$\rho = \frac{1}{3}\omega_Q^2[J(\omega) + 4J(2\omega)], \quad [33]$$

$$\lambda^{22} = \frac{1}{3}\omega_Q^2[J(\omega) + 2J(2\omega)], \quad [34]$$

$$\lambda^{21} = \frac{1}{6}\omega_Q^2[3J(0) + J(\omega) + 2J(2\omega)], \quad [35]$$

$$\rho^2 = \omega_Q^2[J(\omega)], \quad [36]$$

and the dynamic frequency shift contribution is

$$\omega^{\text{dfs}} = \frac{1}{6}\omega_Q^2[L(\omega) + 2L(2\omega)]. \quad [37]$$

The complete homogeneous master equation is obtained by the addition of the coherent part from Eq. [30] and the incoherent relaxation part from Eq. [31]. The inhomogeneous equation system can also be made homogeneous according to the principle presented previously for Eq. [20]. The result is

$$\frac{d}{dt} \begin{bmatrix} \sqrt{2/3}E \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \end{bmatrix} = - \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \lambda & \omega_x & -(\Omega + \omega^{\text{dfs}}) & 0 & 0 & 0 & -\omega_Q & 0 \\ -\sqrt{3/2}M_0\rho & -\omega_x & \rho & \omega_y & 0 & 0 & 0 & 0 & 0 \\ 0 & \Omega + \omega^{\text{dfs}} & -\omega_y & \lambda & 0 & \omega_Q & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \lambda^{22} & -\omega_y & 0 & \omega_x & -2(\Omega + \omega^{\text{dfs}}) \\ 0 & 0 & 0 & -\omega_Q & \omega_y & \lambda^{21} & \sqrt{3}\omega_x & -(\Omega + \omega^{\text{dfs}}) & \omega_x \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{3}\omega_x & \rho^2 & \sqrt{3}\omega_y & 0 \\ 0 & \omega_Q & 0 & 0 & -\omega_x & \Omega + \omega^{\text{dfs}} & -\sqrt{3}\omega_y & \lambda^{21} & \omega_y \\ 0 & 0 & 0 & 0 & 2(\Omega + \omega^{\text{dfs}}) & -\omega_x & 0 & -\omega_y & \lambda^{22} \end{bmatrix} \cdot \begin{bmatrix} \sqrt{2/3}E \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \end{bmatrix} \quad [38]$$

Equation [38] is the complete homogeneous master equation for a spin $S = 1$ nucleus in a Hermitian basis.

The Homogeneous Master Equation for Spin $S = \frac{3}{2}$

The master equation for spin $S = \frac{3}{2}$ can be calculated using the same equations as for spin $S = 1$. After making the equation system homogeneous the result is

$$\frac{d}{dt} \begin{bmatrix} \sqrt{5/4}E \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \\ C_{3,3y} \\ C_{3,2y} \\ C_{3,y} \\ C_{3,z} \\ C_{3,x} \\ C_{3,2x} \\ C_{3,3x} \end{bmatrix} = - \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \lambda & \omega_x & -(\Omega + \omega^{11}) & 0 & 0 & 0 & -\sqrt{12/5}\omega_Q & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\sqrt{4/5}M_0\rho & -\omega_x & \rho & \omega_y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & (\Omega + \omega^{11}) & -\omega_y & \lambda & 0 & 0 & \sqrt{12/5}\omega_Q & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \lambda^{22} & -\omega_y & 0 & \omega_x & -2(\Omega + \omega^{22}) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{12/5}\omega_Q & \omega_y & \lambda^{21} & \sqrt{3}\omega_x & -(\Omega + \omega^{21}) & \omega_x & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{3}\omega_x & \rho^2 & \sqrt{3}\omega_y & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{12/5}\omega_Q & 0 & 0 & 0 & -\omega_x & (\Omega + \omega^{21}) & -\sqrt{3}\omega_y & \lambda^{21} & \omega_y & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & (2\Omega + \omega^{22}) & -\omega_x & 0 & -\omega_y & \lambda^{22} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2\omega_Q \\ 0 & \mu & 0 & -\omega^c & 0 & 0 & 0 & 0 & 0 & -\sqrt{8/5}\omega_Q & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \omega^c & 0 & \mu & 0 & 0 & \sqrt{8/5}\omega_Q & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\omega_Q & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \sqrt{5/4}E \\ C_{1,y} \\ C_{1,z} \\ C_{1,x} \\ C_{2,2y} \\ C_{2,y} \\ C_{2,z} \\ C_{2,x} \\ C_{2,2x} \\ C_{3,3y} \\ C_{3,2y} \\ C_{3,y} \\ C_{3,z} \\ C_{3,x} \\ C_{3,2x} \\ C_{3,3x} \end{bmatrix} \quad [39]$$

with the auto-relaxation rates

$$\lambda = \frac{2}{5}\omega_Q^2[3J(0) + 5J(\omega) + 2J(2\omega)], \quad [40]$$

$$\rho = \frac{4}{5}\omega_Q^2[J(\omega) + 4J(2\omega)], \quad [41]$$

$$\lambda^{22} = 2\omega_Q^2[J(0) + 2J(\omega) + J(2\omega)], \quad [42]$$

$$\lambda^{21} = 2\omega_Q^2[J(0) + J(\omega) + 2J(2\omega)], \quad [43]$$

$$\rho^2 = 4\omega_Q^2[J(\omega) + J(2\omega)], \quad [44]$$

$$\lambda^{33} = 2\omega_Q^2[J(\omega) + J(2\omega)], \quad [45]$$

$$\lambda^{32} = 2\omega_Q^2[J(0) + J(2\omega)], \quad [46]$$

$$\lambda^{31} = \frac{2}{5}\omega_Q^2[2J(0) + 5J(\omega) + 3J(2\omega)], \quad [47]$$

$$\rho^3 = \frac{4}{5}\omega_Q^2[4J(\omega) + J(2\omega)], \quad [48]$$

and the cross-relaxation rates

$$\mu = \frac{2}{5}\sqrt{6}\omega_Q^2[J(0) - J(2\omega)], \quad [49]$$

$$\sigma = \frac{8}{5}\omega_Q^2[J(\omega) - J(2\omega)]. \quad [50]$$

and the dynamic frequency shift contributions

$$\omega^c = \frac{2}{5}\sqrt{6}\omega_Q^2[2L(\omega) - L(2\omega)], \quad [51]$$

$$\omega^{11} = \frac{2}{5}\omega_Q^2[L(\omega) + 2L(2\omega)], \quad [52]$$

$$\omega^{22} = \omega^{32} = 2\omega_Q^2[L(2\omega)], \quad [53]$$

$$\omega^{21} = 2\omega_Q^2[L(\omega)], \quad [54]$$

$$\omega^{33} = 2\omega_Q^2[L(\omega) + L(2\omega)], \quad [55]$$

$$\omega^{31} = \frac{2}{5}\omega_Q^2[-L(\omega) + 3L(2\omega)]. \quad [56]$$

Simulating Pulse Sequences and NMR Spectra

The solution to the homogeneous master equation

$$\frac{d}{dt}\sigma(t) = -P\sigma(t) \quad [57]$$

is

$$\sigma(t = t_1 + \Delta t) = \exp[-P\Delta t]\sigma(t = t_1), \quad [58]$$

where P and σ are the matrix and vector, respectively, in Eqs. [38] and [39].

The observable magnetization can be calculated using (I)

$$\langle \text{Obs} \rangle = \langle \text{Obs}^{\text{Adj.}} | \sigma \rangle, \quad [59]$$

where observable x and y magnetization correspond to the operators $\text{Obs} = S_x$ or S_y , respectively.

DISCUSSION

The off-diagonal anti-symmetric terms in Eq. [30] are due to the coherent part of the Liouville–von Neumann equation. These terms are rotation rates between basis operators induced by the Hamiltonian due to the commutator relationships between the basis operators and the Hamiltonian, Eq. [24].

Information about the relevant commutator relationships for the spin $S = 1$ basis can thus be deduced from the Hamiltonian and the matrix representation of the coherent part of the Liouville–von Neumann equation, Eq. [30]. The term ΩS_z in the Hamiltonian induces rotation between S_x and S_y with the rate Ω according to

$$[S_z, S_x] = iS_y. \quad [60]$$

Cyclic permutations of the commutator relationships responsible for the rotation due to chemical shift are responsible for the rotations induced by the RF field. The chemical shift Hamiltonian does also induce rotation between the x and y magnetization of double-quantum coherence according to

$$[S_z, S_x^2 - S_y^2] = i2(S_x S_y + S_y S_x), \quad [61]$$

i.e., a rotation with twice the Larmor frequency. The quadrupolar Hamiltonian, $\omega_Q(S_z^2 - \frac{1}{3}S^2)$, induces rotation between in-phase and antiphase single-quantum magnetization with the rate ω_Q due to the commutator relationships

$$[S_z^2, S_x] = i(S_y S_z + S_z S_y), \quad [62]$$

$$[S_z^2, S_x S_z + S_z S_x] = iS_y. \quad [63]$$

The incoherent contribution to the master equation consists of two parts. These are the ordinary auto- and cross-relaxation rates from the real part of the spectral density function and the dynamic frequency shifts from the imaginary part of the spectral density function, respectively. The auto-relaxation rates can be found along the diagonal in Eq. [31]. In the particular case of spin $\frac{1}{2}$ or 1 the relaxation matrix includes only auto-relaxation rates in the Hermitian basis. For spin $S > 1$ symmetric off-diagonal cross-relaxation elements also appear in the matrix, see Eq. [39].

The dynamic frequency shift contributions appear in Eq. [31] as anti-symmetric off-diagonal elements. These terms, which are caused by relaxation, occupy the same positions in the matrix as the anti-symmetric elements from the coherent chemical shift terms in Eq. [30]. The dynamic frequency shift thus modifies the position of the resonance as a function of dynamics, as it should.

CONCLUSIONS

We have created a new set of basis operators for any spin quantum number. The basis is Hermitian and includes the unity operator. It is not necessary for the operator basis to be Hermitian since the results of calculations are independent of the choice of base, but there are several advantages with a Hermitian operator basis. The main advantage with a Hermitian operator basis is that the Liouville–von Neumann equation including relaxation does not involve any complex numbers and can be solved using real algebra. This is not true for non-Hermitian operator bases. Real algebra makes numerical calculations faster and simplifies the interpretation of the equation system. The unity operator is included in the basis, which makes it easy to rewrite the Liouville–von Neumann equation from its usual inhomogeneous form into a homogeneous form.

The new basis also forms a natural basis for calculations on coupled spin systems because all the single-spin operators are part of the complete basis when the unity operator is part of the single-spin basis. The advantage is again that the interpretation of the equation system is simplified.

The new Hermitian basis can be viewed as an extension of the Cartesian product operators for spin $S > \frac{1}{2}$ because when Eqs. [5]–[7] are used for spin $S = \frac{1}{2}$ the results are the ordinary Cartesian product operators for a single-spin $E/2$, S_x , S_y , and S_z (3).

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