Direct-product formalism for calculating magnetic resonance signals in many-body systems of interacting spins

Alexander A. Nevzorov and Jack H. Freed[a)]
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853

(Received 9 March 2001; accepted 8 May 2001)

Modern applications of nuclear magnetic resonance and electron spin resonance, and especially quantum computing problems call for more effective formalisms to describe relaxation and evolution of various orders of coherence in the presence of motions of the interacting spins. Here we suggest a formulation for the description of multiquantum spin states based on direct-product structures that take into account the inherent permutation symmetries and quantum coherences of a multispin system. Convenient recursion relations are obtained for the matrix representations of the *N*-body Hamiltonian superoperator and pulse propagators. This allows one to obtain compact expressions for the evolution of magnetic resonance signals when the dipolar interactions amongst spin-bearing molecules are modulated by their motions. These expressions include the free-induction decay and solid echoes, as well as the decay of higher-order coherences under the assumption of statistical independence of the motions of the spin-bearing molecules. Exact results, not requiring this assumption, are obtained for the case of the truncated dipolar Hamiltonian. Important phenomena that arise in multispin systems, such as instantaneous diffusion and spectral diffusion arising from motions, are studied more rigorously by solving the equation for the time evolution of the spin-density states. The many-body magnetic-resonance signals in the presence of motions are obtained by solving the appropriate stochastic Liouville equations. These solutions may be compared to solid-echo experiments to extract translational diffusion coefficients even in the slow motional regime. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1382816]

I. INTRODUCTION

The von Neumann equation for the evolution of the spin-density operator represents the most general way of treating many-spin systems. However, in most cases the conventional treatments restrict its solution either to the solid limit (i.e., when the overall Hamiltonian is time-independent), or to the fast-motional (or Redfield) limit. In the solid limit the solution can be written in terms of matrix transformations of the equilibrium density matrix, whereas in the latter case one usually truncates the formal series solution for the density operator at second-order commutators. In more general treatments, e.g., when motions of the spins become sufficiently slow (or if there is no *a priori* knowledge about their time scale), it becomes necessary to introduce superoperators corresponding to the operation of commutation.[1–6] Therefore, to treat the many-spin problem in a general way, we utilize a matrix representation for the Hamiltonian superoperator (Liouvillian) in order to calculate the time-evolution of the density operator for a many-body system.[7] Naturally, in such a representation the multispin density states (the many-body density matrix) are written as vectors, on which the superoperator matrices (supermatrices) operate.[7] In this case the von Neumann equation for the overall many-body density matrix just becomes a system of coupled linear differential equations which can in principle be solved by standard matrix methods.

In the present paper, hereinafter referred to as Paper I, we suggest a direct-product formalism for calculating magnetic resonance signals in a many-body system of spins 1/2. Direct-product structures allow one to most easily express the interactions amongst various spins in terms of many-body interaction matrices, and can be used to define the multiquantum spin-state vectors, on which these matrices operate. One of the first applications of the direct product for the description of multispin states is found in Onsager's approach to the solution of the two-dimensional Ising model.[8] Direct-product operators have recently been used to represent pure density states[9,10] and the total Hamiltonian operator of a many-spin system.[11] However, algebraic properties of Hamiltonian supermatrices have not been investigated in sufficient detail. Here we factorize matrix representations for the Zeeman and dipolar superoperators into direct (or Kronecker) products[8] in terms of convenient recursion relations. We show that, in the eigenoperator basis of the unperturbed Zeeman Hamiltonian superoperator,[1] the multispin density states can also be factorized in terms of direct-product structures that naturally take into account all possible multiquatnum coherences. As will be shown by several examples, such a formalism allows one to calculate the magnetic resonance signals in various cases by merely applying the main multiplication property of the direct product to superoperators as many times as needed, viz., $(\mathbf{A}\otimes\mathbf{B})(\mathbf{a}\otimes\mathbf{b})=(\mathbf{Aa})\otimes(\mathbf{Bb})$. As an illustration of the method, we rederive the earlier result[7] for the free induction decay (FID) arising in a system of identical interacting spins of 1/2 by applying the direct-

a)Electronic mail: jhf@ccmr.cornell.edu

product methodology in conjunction with generalized cumulant expansions.[2,7,12]

Most modern NMR and ESR experiments are not limited to just the acquisition of the free-induction decay (FID) signal. However, the calculation of multiple-pulse sequences by conventional methods often yields results that are too difficult to study analytically, especially in many-body systems. This also includes the evolution of higher-order multiple quantum coherences produced by the pulses, a matter that was too complicated to be successfully treated by our earlier method.[7] Therefore, the formalism is further developed in order to include the effects of additional pulses. The solid-echo and Hahn echo pulse sequences in a many-body system of identical spins are analyzed from first principles giving rise to motionally generated spectral diffusion and the phenomenon of instantaneous diffusion.[13] We also investigate the relaxation of multiple quantum coherences. Exact results are obtained for a truncated dipolar Hamiltonian, i.e., containing the $I_z^{(i)}I_z^{(j)}$ terms only. When the assumption of stochastic independence of the motions of the spin-bearing molecules is made as in Ref. 7, then the results are generalized for the complete secular dipolar Hamiltonian, i.e., involving the $\frac{3}{2}I_z^{(i)}I_z^{(j)}-\frac{1}{2}\mathbf{I}^{(i)}\mathbf{I}^{(j)}$ terms.[14]

We wish to emphasize that only through the formalism developed in this paper has it been possible to generate key new results in this work and in an accompanying work[15] hereinafter referred to as Paper II. Despite our frequent use of the assumption of stochastic independence of motions (SIM) the many-body spin system is a formidable one, especially when taken over the whole motional range. Only by the new methodology have we been able to provide the correct results for spin-echo experiments, which necessarily involves the effects of higher order coherences. As we noted in our previous work,[7] these results are required to analyze such experiments in solutions of like spins of 1/2, where the dipolar interaction is significant, and where the slow motional regime is achieved, e.g., for ESR studies on radicals in moderately viscous fluids (i.e., where $D_T<10^{-6}$ cm^2/s, where D_T is the translational diffusion coefficient for relative diffusion of two spin-bearing molecules). Our new results supersede the overly approximate results of Ref. 7.

The assumption of SIM is to our mind appropriate for discussing fluids: Nonviscous, viscous, or frozen. As we have previously shown, our theory bridges the gap between the two limiting theories for the continuous wave (cw) linewidths: Motional narrowing theory and the Anderson statistical model for dilute spin systems.[14] These classic theories are based on the *Ansatz* of independently summing up the effects of two-body interactions. Our results, appropriate over the whole motional range, show that the SIM assumption is sufficient to recover these limiting theories. Thus, while retaining this assumption, we also explore the results for more concentrated solutions, which take the (near) solid-state lineshapes from Lorentzian to Gaussian.

In Paper II, the direct-product formalism is used to describe spin relaxation in an $A-B_N$ system, e.g., an electron spin bearing molecule dissolved in a solvent of proton containing molecules. The direct-product formalism was essential for us to obtain all the results reported therein, given the more complicated spin-Hamiltonian, which includes off-resonance effects and multiquantum transitions of the B_N system. In addition to describing the effects of motional modulation of the many-body dipolar interactions on the A spin using the SIM assumption, we also treat the coherent effects of "spin-diffusion" in a solid crystalline lattice of B spins, wherein the SIM assumption is inapplicable. This case clearly shows the value of the direct-product formalism for coherent many-body problems.

II. THE EIGENOPERATOR METHOD FOR SOLVING THE DENSITY-MATRIX EQUATION

We seek the solution of the density matrix equation,

$$\frac{\partial\rho(t)}{\partial t}=-i[H,\rho(t)]=-i[H_0,\rho(t)]-i\sum_{i<j}^{N}[H^{(ij)},\rho(t)], \tag{2.1}$$

in the form[7]

$$\rho(t)=\sum_{\{\epsilon\}}g_{\{\epsilon\}}(t)E_{\{\epsilon\}}. \tag{2.2}$$

Here the pairwise interaction Hamiltonians $H^{(ij)}$ may be in general time-dependent, the spin-density coefficients $g_{\{\epsilon\}}(t)$ are some functions of time as well, and the $E_{\{\epsilon\}}$ are a set of basis operators with a numbering scheme $\{\epsilon\}$ that is introduced in the next section. For a system of N particles of spin 1/2, operators $E_{\{\epsilon\}}$ can be written as a product of N spin operators,[16] each acting on its own spin i,

$$E_{\{\epsilon\}}=\prod_{i=1}^{N}I_{\epsilon_i}^{(i)}. \tag{2.3}$$

Here $\{\epsilon\}$ denotes a permutation set, $\{\epsilon\}=\{\epsilon_1,\epsilon_2,\ldots\epsilon_N\}$, $\epsilon_i=+$, α, β, or $-$, I_+ and I_- are the conventional raising and lowering spin operators, and the polarization operators I_α and I_β are defined as[1]

$$I_\alpha=\tfrac{1}{2}+I_z, \quad I_\beta=\tfrac{1}{2}-I_z. \tag{2.4}$$

As follows from the trace properties of I_+, I_-, I_α, and I_β, the operators of Eq. (2.3) form a complete orthonormal basis set in operator space with the Frobenius trace metric defined as

$$(E_{\{\epsilon\}},E_{\{\epsilon'\}})\equiv\mathrm{Tr}(E_{\{\epsilon\}}^{\dagger}E_{\{\epsilon'\}})=\delta_{\{\epsilon\},\{\epsilon'\}}, \tag{2.5}$$

where the dagger † denotes the Hermitian conjugate.

Let us consider the following dipolar interaction Hamiltonian:

$$\begin{aligned}H^{(ij)}&=\chi F(\mathbf{r}_{ij})[I_z^{(i)}I_z^{(j)}-\tfrac{1}{4}(I_+^{(i)}I_-^{(j)}+I_-^{(i)}I_+^{(j)})],\\ F(\mathbf{r}_{ij})&\equiv\frac{Y_0^{(2)}(\Omega_{ij})}{r_{ij}^3},\end{aligned} \tag{2.6}$$

where $\chi\equiv\sqrt{(16\pi/5)}/\gamma^2\hbar$ is the coupling constant, r_{ij} is the distance between the ith and jth spins, and Ω_{ij} is the orientation of the vector $\mathbf{r}_{ij}$ connecting the two spins with respect to the main magnetic field. Here the time dependence of $H^{(ij)}$ may be implicitly contained in the classical variables $\mathbf{r}_{ij}$. By using the orthogonality property of the eigenopera-

tors, one obtains an equivalent of the von Neumann equation for the density matrix in the eigenoperator representation that couples the functions $g_{\{\epsilon\}}(t)$. That is

$$\frac{\partial g_{\{\epsilon\}}(t)}{\partial t} = -i\sum_{\{\epsilon'\}}\left[\Delta\Omega_{\{\epsilon\}\{\epsilon'\}} + \chi\sum_{i<j}^{N} C^{(ij)}_{\{\epsilon\}\{\epsilon'\}} F(\mathbf{r}_{ij})\right] \times g_{\{\epsilon'\}}(t). \tag{2.7}$$

Here the (diagonal) matrix of frequency offsets $\Delta\Omega$ is the representation of the Zeeman–Hamiltonian superoperator in its eigenoperator basis, and is given by

$$\Delta\Omega_{\{\epsilon\}\{\epsilon'\}} = \delta_{\{\epsilon\}\{\epsilon'\}}\mathrm{Tr}(E^{\dagger}_{\{\epsilon\}}[H_0, E_{\{\epsilon'\}}]). \tag{2.8}$$

The matrix $\mathbf{C}^{(ij)}$ represents the interaction Hamiltonian between spin i and spin j in the eigenoperator basis, and is defined by

$$\chi C^{(ij)}_{\{\epsilon\}\{\epsilon'\}} F(\mathbf{r}_{ij}) = \mathrm{Tr}(E^{\dagger}_{\{\epsilon\}}[H^{(ij)}, E_{\{\epsilon'\}}]). \tag{2.9}$$

The explicit form of $\mathbf{C}^{(ij)}$ clearly depends on the commutation relations between the basis operators and the interaction Hamiltonian, $H^{(ij)}$.

Equation (2.7) allows one to formally solve for the evolution of the motionally averaged (over all realizations of a Brownian motion, e.g., translational diffusion in variables $\mathbf{r}_{ij}$) components of the density matrix in the eigenoperator representation even if the interaction is *time-dependent*, viz.,

$$\mathbf{g}(t) = \left\langle e^{-i\Delta\Omega t - i\chi\Sigma_{i_1<j_1}^{N}\mathbf{C}^{(i_1 j_1)}\int_0^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1))}_{O}\right\rangle \mathbf{g}(0). \tag{2.10}$$

Here the symbol "O" stands for the Dyson time-ordering, which accounts for the fact that the superoperator matrices may not commute at different times, and the triangular brackets denote motional averaging.

III. DIRECT-PRODUCT REPRESENTATION OF SUPEROPERATOR MATRICES AND SPIN-DENSITY STATES IN THE *N*-BODY PROBLEM

The first step in constructing the matrices for the Hamiltonian superoperator and the vector describing the initial spin-density state (which we shall call the starting vector) is the choice of the bookkeeping scheme for the eigenoperators $E_{\{\epsilon\}}$. As a numbering scheme for the eigenoperators we choose a quaternary tree structure constructed by analogy with binary trees as depicted in Fig. 1. The spins are numbered from the left to the right, i.e., the first operator is understood to act on spin 1, the second—on spin 2, etc. The index $\boldsymbol{\epsilon}$ runs from the top to the bottom at a given N, and one can, therefore, omit the curly brackets in Eqs. (2.7)–(2.9), since $\boldsymbol{\epsilon}$ is no longer a permutation set but a consecutive numbering index according to the method of generating the quaternary tree. Note that the "length" of each eigenoperator (i.e., the number of single-spin operators) is constant and is equal to N. Note also that the ordering for individual spin operators is chosen to be: I_+, I_α, I_β, I_-.

We start with defining the properties of the vector space of time-dependent *multispin density states* $\mathbf{g}(t)$ on which the Ω and C-matrices operate. In general, a density-state vector

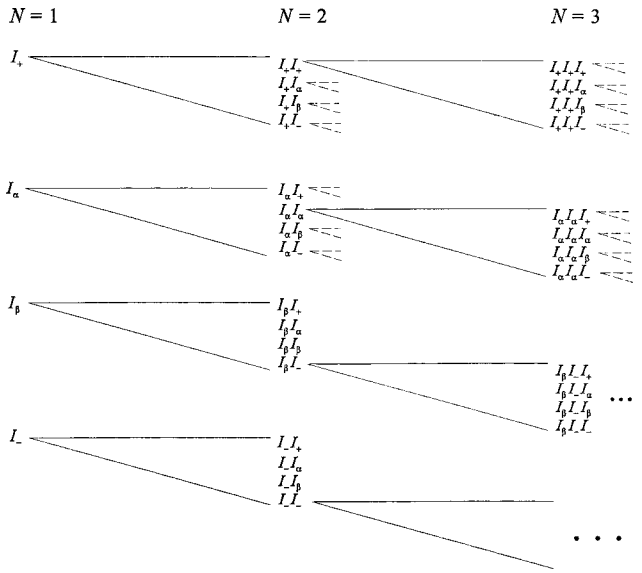

FIG. 1. Quaternary tree numbering scheme for constructing the eigenoperator basis for the Hamiltonian superoperator representation.

for an N-spin problem shall be sought as a linear combination of direct-product structures each of them having length N, viz.,

$$\mathbf{g}_N(t) = \sum_{\epsilon_1,\epsilon_2,\ldots\epsilon_N} f_{\epsilon_1,\epsilon_2,\ldots\epsilon_N}(t)\mathbf{i}_{\epsilon_1}\otimes\mathbf{i}_{\epsilon_2}\otimes\cdots\otimes\mathbf{i}_{\epsilon_N}, \tag{3.1}$$

where the coefficients $f_{\epsilon_1,\epsilon_2,\ldots\epsilon_N}(t)$ are functions of time and $\epsilon_i = +$, α, β, or $-$ for spins of 1/2, by analogy with Eq. (2.3). Here the symbol "$\otimes$" is used to designate the direct (or tensor, or outer, or Kronecker) product. Specifically, for any two matrices $\mathbf{A}$ and $\mathbf{B}$ of any size (including vectors) the direct product is defined by[17]

$$\mathbf{A}\otimes\mathbf{B} \equiv \begin{pmatrix} a_{11}\mathbf{B} & a_{12}\mathbf{B} & \cdots & a_{1n}\mathbf{B} \\ \vdots & \vdots & \vdots & \vdots \\ a_{m1}\mathbf{B} & a_{m2}\mathbf{B} & \cdots & a_{mn}\mathbf{B} \end{pmatrix}. \tag{3.2}$$

We have also introduced the density-state vectors $\mathbf{i}_\epsilon$ corresponding to each individual spin that are defined, according to the chosen ordering of the operators I_+, I_α, I_β, and I_- for spins of 1/2 by

$$\mathbf{i}_+ = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix};\ \mathbf{i}_\alpha = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix};\ \mathbf{i}_\beta = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix};\ \mathbf{i}_- = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{3.3}$$

Let us consider a system of N equivalent spins of 1/2, removed from equilibrium by an initial nonselective $(\pi/2)_x$ pulse. Let us call the difference between the number of operators I_+ and the number of operators I_- in a given eigenoperator the *order of coherence*[18] of this eigenoperator, μ. Clearly, the presence of the operators I_α or I_β does not affect μ. In the high-temperature approximation, the starting vector $\mathbf{g}_N(0)$ corresponding to the eigenoperators that have only

one operator $I_+(\mu=+1)$ and all possible combinations of operators I_α and I_β, is readily seen to be given for $N+1$ spins in terms of the recursion formula

$$\mathbf{g}_{N+1}^{(+1)}(0)=(\mathbf{i}_\alpha+\mathbf{i}_\beta)\otimes\mathbf{g}_N^{(+1)}(0)+\mathbf{i}_+\otimes\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N, \tag{3.4}$$

where the second term on the right gives the contribution of $\mathbf{i}_+$ from the $N+1$th spin, and the first term just increases the product operator dimension from 4^N to 4^{N+1}. There is also a counter-rotating component corresponding to $\mu=-1$ which can be considered separately from the $\mu=1$ component for calculating a pure FID signal. For the sake of compactness of notation, we shall further omit the index μ whenever possible and include it as a superscript only when it becomes necessary. We have also used curly bracket notation to designate the direct product repeated N times,

$$\{\mathfrak{R}\}^N\equiv\underbrace{\mathfrak{R}\otimes\mathfrak{R}\otimes\cdots\otimes\mathfrak{R}}_{N\ \text{times}}=\mathfrak{R}\prod_{m=1}^{N-1}\otimes\mathfrak{R}. \tag{3.5}$$

The recursion formula, Eq. (3.4), has a simple meaning. On the one hand, it is easy to see that (in the high-temperature approximation) the starting vector in the direct-product representation having $\mu=+1$ corresponds to the sum $\Sigma_{i=1}^N I_+^{(i)}$ in the usual spin-operator space (since $I_\alpha+I_\beta=\mathbf{1}$). On the other hand, by adding one more spin to the system, $N\rightarrow N+1$, we increase the dimension of the space by a factor of 4. Since the total order of coherence is constant (i.e., $\mu=+1$), we shall only have products of $\mathbf{g}_N(0)$ with $\mathbf{i}_\alpha+\mathbf{i}_\beta$, the latter term adding no coherences, and $\mathbf{i}_+$ with all possible combinations of $\mathbf{i}_\alpha$ and $\mathbf{i}_\beta$ as given by the direct-product binomial $\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N$. By applying the recursion relation $N-1$ times, the general formula for the initial multispin density-state vector becomes

$$\mathbf{g}_N(0)=\sum_{m=0}^{N-1}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^m\otimes\mathbf{i}_+\otimes\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^{N-1-m}. \tag{3.6}$$

Direct-product structures of the above type (i.e., $\Sigma_k\{\mathbf{A}\}^k\otimes\mathbf{B}\otimes\{\mathbf{A}\}^{N-k}$) we shall call the ''dressed direct-product sums.'' Thus, the starting vector for the N-body problem consists of a sum of N direct-product structures, each of them having ''length'' N.

The matrices corresponding to the interaction Hamiltonian superoperator in the eigenoperator representation are also given by a recursion formula as

$$\begin{aligned}\sum_{i<j}^{N+1}\chi\mathbf{C}_{N+1}^{(ij)}F(\mathbf{r}_{ij})&=\mathbf{E}\otimes\sum_{2\leqslant i<j}^{N+1}\chi\mathbf{C}_N^{(ij)}F(\mathbf{r}_{ij})\\&\quad+\sum_{m=1}^{N}\Pi_m(\chi\mathbf{C}_2\otimes\{\mathbf{E}\}^{N-1})\Pi_m^{-1}F(\mathbf{r}_{1m+1}).\end{aligned} \tag{3.7}$$

The above equation has again a rather clear meaning: Addition of a new spin increases the size of the spin space by a factor of 4 (which is taken care of in terms of the direct multiplication by the 4×4 unit matrix $\mathbf{E}$ from the left) plus N additional permutations to account for the interactions of the ''new'' spin (''spin 1'') with the remaining N spins located at positions $\mathbf{r}_{1m+1}$ relative to spin 1. In Eq. (3.7), the matrix $\mathbf{C}_2$ is the two-spin 16 by 16 interaction matrix, the elements of which can be found by explicitly calculating the commutators of the interaction Hamiltonian with the eigenoperators, Eq. (2.9). For instance, for the case of the dipolar interaction, Eq. (2.6), $\mathbf{C}_2$ is given by

$$\mathbf{C}_2=\begin{pmatrix}
1/2 & & & 1/4 & & & & & & & & & & & & \\
 & -1/2 & & & & & & -1/4 & & & & & & & & \\
 & & & & 1/4 & & & & -1/4 & & & & & & & \\
1/4 & & & 1/2 & & & & & & & & & & & & \\
 & & 1/4 & & & & & & & & & -1/4 & & & & \\
 & & & & & & -1/2 & & & & & & -1/4 & & & \\
 & -1/4 & & & & & & -1/2 & & & & & & & & \\
 & & -1/4 & & & & & & & & & 1/4 & & & & \\
 & & & & & & & & & 1/2 & & & & & 1/4 & \\
 & & & & -1/4 & & & & 1/4 & & & & & & & \\
 & & & & & & -1/4 & & & & & & -1/2 & & & \\
 & & & & & & & & & 1/4 & & & & & 1/2 &
\end{pmatrix}
\begin{matrix}
I_+^{(1)}I_+^{(2)}\\ I_+^{(1)}I_\alpha^{(2)}\\ I_+^{(1)}I_\beta^{(2)}\\ I_+^{(1)}I_-^{(2)}\\
I_\alpha^{(1)}I_+^{(2)}\\ I_\alpha^{(1)}I_\alpha^{(2)}\\ I_\alpha^{(1)}I_\beta^{(2)}\\ I_\alpha^{(1)}I_-^{(2)}\\
I_\beta^{(1)}I_+^{(2)}\\ I_\beta^{(1)}I_\alpha^{(2)}\\ I_\beta^{(1)}I_\beta^{(2)}\\ I_\beta^{(1)}I_-^{(2)}\\
I_-^{(1)}I_+^{(2)}\\ I_-^{(1)}I_\alpha^{(2)}\\ I_-^{(1)}I_\beta^{(2)}\\ I_-^{(1)}I_-^{(2)}
\end{matrix}, \tag{3.8}$$

where we have included the corresponding eigenoperators on the right side to indicate their ordering scheme. We shall not make much use of the explicit form for the matrix $\mathbf{C}_2$, but will exploit in more detail its eigensystem (cf. the next section). Now, Π_m are 4^{N+1} by 4^{N+1} permutation matrices such that

$$\begin{aligned}
&\Pi_1 = \mathbf{1},\\
&\Pi_2 = \mathbf{P}_{23},\\
&\Pi_3 = \mathbf{P}_{34}\mathbf{P}_{23},\\
&\Pi_4 = \mathbf{P}_{45}\mathbf{P}_{34}\mathbf{P}_{23},\\
&\cdots,\\
&\Pi_N = \mathbf{P}_{N+1N}\mathbf{P}_{NN-1}\cdots\mathbf{P}_{23}.
\end{aligned} \tag{3.9}$$

Here the role of individual matrices $\mathbf{P}_{ii+1}$ is to permute the ith and $i+1$th elements, numbered from the left, in a direct-product sequence consisting of several subvectors $\mathbf{a}_i$ of length 4, viz.,

$$\mathbf{P}_{ii+1}\mathbf{a}_1\otimes\cdots\otimes\mathbf{a}_i\otimes\mathbf{a}_{i+1}\otimes\cdots = \mathbf{a}_1\otimes\cdots\otimes\mathbf{a}_{i+1}\otimes\mathbf{a}_i\otimes\cdots. \tag{3.10}$$

Equation (3.7) can be illustrated for the case of three spins leading to three distinct pairwise interaction C-matrices. They will be acting on coherent spin states given by direct product structures of the form $\mathbf{a}\otimes\mathbf{b}\otimes\mathbf{c}$ (describing various multispin states of the many-body system), where the ordering corresponds to spins 1, 2, and 3, respectively. The matrices $\mathbf{C}^{(1,2)}$ and $\mathbf{C}^{(2,3)}$ are self-evident, and are given by

$$\mathbf{C}^{(1,2)} = \mathbf{C}_2\otimes\mathbf{E}, \quad \mathbf{C}^{(2,3)} = \mathbf{E}\otimes\mathbf{C}_2. \tag{3.11}$$

The remaining matrix $\mathbf{C}^{(1,3)}$ can be obtained from matrix $\mathbf{C}^{(1,2)}$, for example, by permuting spins 2 and 3 in the vector $\mathbf{a}\otimes\mathbf{b}\otimes\mathbf{c}$ first, then acting by the matrix $\mathbf{C}^{(1,2)}$, and then permuting spins 2 and 3 again to return to the original numbering scheme. This is equivalent to transforming the matrix $\mathbf{C}^{(1,2)}$ as

$$\begin{aligned}
\mathbf{C}^{(1,3)} &= \Pi_2\mathbf{C}^{(1,2)}\Pi_2^{-1}\\
&= \Pi_2(\mathbf{C}_2\otimes\mathbf{E})\Pi_2^{-1}\\
&= (\mathbf{E}\otimes\mathbf{P})(\mathbf{C}_2\otimes\mathbf{E})(\mathbf{E}\otimes\mathbf{P}),
\end{aligned} \tag{3.12}$$

where $\mathbf{P}$ is a 16×16 permutation matrix such that

$$\mathbf{P}(\mathbf{a}\otimes\mathbf{b}) = \mathbf{b}\otimes\mathbf{a}, \quad \mathbf{P}(\mathbf{A}\otimes\mathbf{B})\mathbf{P}^{-1} = \mathbf{B}\otimes\mathbf{A}, \tag{3.13}$$

for any four-dimensional (4D) vectors $\mathbf{a}$ and $\mathbf{b}$, and for any 4×4 matrices $\mathbf{A}$ and $\mathbf{B}$. The matrix $\mathbf{P}$ is explicitly given by

$$\mathbf{P} = \begin{pmatrix}
1 & & & & & & & & & & & & & & & \\
 & & 1 & & & & & & & & & & & & & \\
 & & & & & & 1 & & & & & & & & & \\
 & & & & & & & & & & & & 1 & & & \\
 & 1 & & & & & & & & & & & & & & \\
 & & & & 1 & & & & & & & & & & & \\
 & & & & & & & & 1 & & & & & & & \\
 & & & & & & & & & & & & & & & 1 \\
 & & & 1 & & & & & & & & & & & & \\
 & & & & & & & & & & 1 & & & & & \\
 & & & & & & & & & & & & & 1 & & \\
 & & & & & & & & & & & & & & 1 & \\
 & & & & & 1 & & & & & & & & & & \\
 & & & & & & & & & & & 1 & & & & \\
 & & & & & & & & & & & & 1 & & & \\
 & & & & & & & & & & & & & & & 1
\end{pmatrix}. \tag{3.14}$$

Note that clearly $\mathbf{P}\mathbf{C}_2\mathbf{P}^{-1} = \mathbf{C}_2$ since interchanging the two spins does not change anything in a two-body interaction, $\mathbf{C}_2 = \mathbf{C}_2^T$. Again, the explicit form of the matrix $\mathbf{P}$ will not be used here; it is sufficient to know that such a matrix exists.

Thus, together with the 4 by 4 unit matrix ($\mathbf{E}$), $\mathbf{C}_2$ *and* $\mathbf{P}$ *fully determine all the possible interactions in a multi-spin system*.

For N identical spins, one has clearly for any m

$$\Pi_m\mathbf{g}_N(0) = \mathbf{g}_N(0), \tag{3.15}$$

since the direct product structure of the starting vector given by Eq. (3.6) is invariant under any permutation of the spins.

It can be checked directly that the matrix representation of the two-body dipolar superoperator, Eq. (3.8), correspond-

ing to the Hamiltonian $I_z^{(1)}I_z^{(2)}-1/4(I_+^{(1)}I_-^{(2)}+I_-^{(1)}I_+^{(2)})$, can be factorized in terms of direct products of 4-by-4 matrices, viz.,

$$\mathbf{C}_2=(I_z\otimes\mathbf{e})\otimes(I_z\otimes\mathbf{e})-(\mathbf{e}\otimes I_z)\otimes(\mathbf{e}\otimes I_z)-\tfrac{1}{4}[(I_+\otimes\mathbf{e})\otimes(I_-\otimes\mathbf{e})-(\mathbf{e}\otimes I_+)\otimes(\mathbf{e}\otimes I_-)$$
$$+(I_-\otimes\mathbf{e})\otimes(I_+\otimes\mathbf{e})-(\mathbf{e}\otimes I_-)\otimes(\mathbf{e}\otimes I_+)], \tag{3.16}$$

where $\mathbf{e}$ is a 2-by-2 unit matrix. Thus, the N-body superoperator in 4^N dimensions represents the dressed sum of $3N(N-1)/2$ direct products, each of them having the corresponding operators at positions i and j. That is

$$\mathbf{H}_\epsilon^{(ij)x}=\chi_\epsilon F(\mathbf{r}_{ij})[\mathbf{E}\otimes\cdots\mathbf{E}\otimes(I_\epsilon\otimes\mathbf{e})\otimes\mathbf{E}\otimes\cdots\mathbf{E}\otimes(I_\epsilon^T\otimes\mathbf{e})\otimes\mathbf{E}\cdot\cdots\otimes\mathbf{E}$$
$$-\mathbf{E}\otimes\cdots\mathbf{E}\otimes\underbrace{(\mathbf{e}\otimes I_\epsilon)}_{i\text{th position}}\otimes\mathbf{E}\otimes\cdots\mathbf{E}\otimes\underbrace{(\mathbf{e}\otimes I_\epsilon^T)}_{j\text{th position}}\otimes\mathbf{E}\cdot\cdots\otimes\mathbf{E}], \tag{3.17}$$

where $\epsilon=z$, $+$, or $-$, $\chi_\epsilon=\chi$ for $\epsilon=z$ and is $(-\chi/4)$ otherwise, and the symbol T designates the matrix transpose.

IV. MANY-BODY FID AND EFFECTS OF THE EXCHANGE TERMS

In this section, we shall re-derive the solution to the motionally averaged free-induction decay signal of Eq. (2.10), which can be performed more efficiently (and more elegantly) by using the direct-product formalism as compared to its initial derivation in Appendix I of Ref. 7. We shall show that the starting vector has very simple eigenvalue properties in the case of nonselective excitation (like spins).

For practical purposes, it is convenient to break the dipolar Hamiltonian superoperator, Eq. (3.16), into the sum of the diagonal and the exchange parts

$$\mathbf{C}_2=\mathbf{C}_2^{\text{diag}}+\mathbf{C}_2^{\text{ex}}, \tag{4.1a}$$

where

$$\mathbf{C}_2^{\text{diag}}=\tfrac{3}{2}[(I_z\otimes\mathbf{e})\otimes(I_z\otimes\mathbf{e})-(\mathbf{e}\otimes I_z)\otimes(\mathbf{e}\otimes I_z)],$$
$$\mathbf{C}_2^{\text{ex}}=-\tfrac{1}{2}\{(I_z\otimes\mathbf{e})\otimes(I_z\otimes\mathbf{e})-(\mathbf{e}\otimes I_z)\otimes(\mathbf{e}\otimes I_z)$$
$$+\tfrac{1}{2}[(I_+\otimes\mathbf{e})\otimes(I_-\otimes\mathbf{e})-(\mathbf{e}\otimes I_+)\otimes(\mathbf{e}\otimes I_-)$$
$$+(I_-\otimes\mathbf{e})\otimes(I_+\otimes\mathbf{e})-(\mathbf{e}\otimes I_-)\otimes(\mathbf{e}\otimes I_+)]\}. \tag{4.1b}$$

Note that in the usual operator notation this separation is equivalent to writing the Hamiltonian of Eq. (2.6) as

$$H^{(ij)}=H^{\text{diag}(ij)}+H^{\text{ex}(ij)}=\tfrac{3}{2}\chi F(\mathbf{r}_{ij})[I_z^{(i)}I_z^{(j)}-\tfrac{1}{3}\mathbf{I}^{(i)}\mathbf{I}^{(j)}]. \tag{4.2}$$

These parts have the following properties with respect to the spin-density states, which can be checked directly from Eq. (4.1b):

$$\mathbf{C}_2^{\text{diag}}\mathbf{i}_\pm\otimes\mathbf{i}_\alpha=\pm\tfrac{3}{4}\mathbf{i}_\pm\otimes\mathbf{i}_\alpha, \tag{4.3a}$$

$$\mathbf{C}_2^{\text{diag}}\mathbf{i}_\pm\otimes\mathbf{i}_\beta=\mp\tfrac{3}{4}\mathbf{i}_\pm\otimes\mathbf{i}_\beta, \tag{4.3b}$$

$$\mathbf{C}_2^{\text{diag}}\mathbf{i}_\alpha\otimes\mathbf{i}_\beta=\mathbf{0}, \tag{4.3c}$$

$$\mathbf{C}_2^{\text{diag}}\mathbf{i}_+\otimes\mathbf{i}_-=\mathbf{0}, \tag{4.3d}$$

$$\mathbf{C}_2^{\text{ex}}\mathbf{i}_\pm\otimes\mathbf{i}_\alpha=\mp\tfrac{1}{4}[\mathbf{i}_\pm\otimes\mathbf{i}_\alpha-\mathbf{i}_\alpha\otimes\mathbf{i}_\pm], \tag{4.3e}$$

$$\mathbf{C}_2^{\text{ex}}\mathbf{i}_\pm\otimes\mathbf{i}_\beta=\pm\tfrac{1}{4}[\mathbf{i}_\pm\otimes\mathbf{i}_\beta-\mathbf{i}_\beta\otimes\mathbf{i}_\pm], \tag{4.3f}$$

$$\mathbf{C}_2^{\text{ex}}\mathbf{i}_\alpha\otimes\mathbf{i}_\beta=\tfrac{1}{4}[\mathbf{i}_+\otimes\mathbf{i}_--\mathbf{i}_-\otimes\mathbf{i}_+], \tag{4.3g}$$

$$\mathbf{C}_2^{\text{ex}}\mathbf{i}_+\otimes\mathbf{i}_-=\tfrac{1}{4}[\mathbf{i}_\alpha\otimes\mathbf{i}_\beta-\mathbf{i}_\beta\otimes\mathbf{i}_\alpha]. \tag{4.3h}$$

It is important to note that the exchange terms result in antisymmetric direct-product combinations with respect to interchanging the two spins. Other important relations are

$$\mathbf{C}_2^{\text{diag,ex}}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^2=\mathbf{C}_2^{\text{diag,ex}}\mathbf{i}_{\alpha,\beta}\otimes\mathbf{i}_{\alpha,\beta}$$
$$=\mathbf{C}_2^{\text{diag,ex}}\mathbf{i}_{+,-}\otimes\mathbf{i}_{+,-}=\mathbf{0}, \tag{4.4}$$

where the density-state vectors for individual spins, $\mathbf{i}_{+,-}$ and $\mathbf{i}_{\alpha,\beta}$ are defined in Eq. (3.3), and the two-body supermatrices $\mathbf{C}_2^{\text{diag,ex}}$ are given by Eq. (4.1b). For N identical spins of 1/2, the starting vector $\mathbf{g}_N(0)$ corresponding to $\mu=\pm1$, Eq. (3.6), can be decomposed into a sum of orthogonal vectors $\mathbf{g}_{l,N}(0)$

$$\mathbf{g}_N(0)=\sum_l\ \sum_{\text{over all permutations}}$$
$$\mathbf{i}_+\otimes\underbrace{\mathbf{i}_\alpha\otimes\mathbf{i}_\alpha\otimes\cdots\otimes\mathbf{i}_\alpha}_{l\text{ vectors}}\otimes\mathbf{i}_\beta\otimes\mathbf{i}_\beta\otimes\cdots\otimes\mathbf{i}_\beta$$
$$=\sum_{l=0}^{N-1}\mathbf{g}_{l,N}(0), \tag{4.5}$$

where l denotes the number of vectors $\mathbf{i}_\alpha$ in each of the direct products of length N of which $\mathbf{g}_{l,N}(0)$ is composed. It is then easy to show that, for the case of a nonselective excitation (like spins), the exchange terms have a vanishing effect on the starting vector $\mathbf{g}_N(0)$, cf. Eqs. (4.3e)–(4.3g). That is, for any i and j we have: $\mathbf{C}^{\text{ex}(ij)}\mathbf{g}_{l,N}(0)=\mathbf{0}$, since the corresponding states $\mathbf{i}_\pm$, $\mathbf{i}_\alpha$, and $\mathbf{i}_\beta$, occur in $\mathbf{g}_{l,N}(0)$ in all possible symmetric permutations. More generally, for *any* vectors $\mathbf{a}$ and $\mathbf{b}$ we have

$$\mathbf{C}_2^{\text{ex}}(\mathbf{a}\otimes\mathbf{b}+\mathbf{b}\otimes\mathbf{a})=\mathbf{0}. \tag{4.6}$$

By using the cumulant expansion[2,3,12] of the exponential operator of Eq. (2.10), one can calculate the FID signal for a system of interacting spins of 1/2, if the motions of the spins are stochastically independent, cf. Ref. 7

$$\frac{G(t)}{Z}=\mathbf{g}_N^T(0)\langle e_O^{-i\mathbf{\Delta\Omega}t-i\chi\Sigma_{i_1<j_1}^N\mathbf{C}^{(i_1j_1)}\int_0^t dt_1F(\mathbf{r}_{i_1j_1}(t_1))}\rangle\mathbf{g}_N(0)$$

$$=\mathbf{g}_N^T(0)\,\exp_O\Bigg\{\sum_{n=1}^{\infty}(-i\chi)^n\sum_{i<j}^{N}[\mathbf{C}^{(ij)}]^n\times\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\times\langle F(\mathbf{r}(t_1))F(\mathbf{r}(t_2))\cdots F(\mathbf{r}(t_n))\rangle_c\Bigg\}\mathbf{g}_N(0). \quad (4.7)$$

Here $Z\equiv 2^{-N}\hbar\omega/kT\equiv 2^{-N}q$, the factor arising from the high-temperature expansion of the equilibrium density matrix. Since $\mathbf{C}^{\mathrm{diag}(ij)}$ and $\mathbf{C}^{\mathrm{ex}(ij)}$ commute for the same i and j, we can use the binomial expansion,

$$[\mathbf{C}^{(ij)}]^n=\sum_{p=0}^{N}\binom{n}{p}[\mathbf{C}^{\mathrm{diag}(ij)}]^{n-p}[\mathbf{C}^{\mathrm{ex}(ij)}]^p. \quad (4.8)$$

But from Eq. (4.6) it follows that only the terms with $p=0$ survive, a consequence of the assumption of stochastically independent motions in Eq. (4.7). Application of Eqs. (4.3a)–(4.3c) and (4.4) directly gives the eigenvector properties of the components $\mathbf{g}_{l,N}(0)$ of the starting vector $\mathbf{g}_N(0)$,

$$\sum_{i<j}^{N}[\mathbf{C}^{(ij)}]^n\mathbf{g}_{l,N}(0)=\sum_{i<j}^{N}[\mathbf{C}^{\mathrm{diag}(ij)}]^n\mathbf{g}_{l,N}(0)=l(+\tfrac{3}{4})^n+(N-1-l)(-\tfrac{3}{4})^n]\mathbf{g}_{l,N}(0), \quad (4.9)$$

since for a given vector $\mathbf{g}_{l,N}(0)$ there will be l terms corresponding to pairs $\mathbf{i}_+\otimes\mathbf{i}_\alpha$, each yielding a factor of $(+3/4)^n$, and $N-l-1$ terms corresponding to pairs $\mathbf{i}_+\otimes\mathbf{i}_\beta$, each yielding a factor of $(-3/4)^n$.

The above eigenvalue property of the starting vector also means that there are no new orders of coherence produced during the evolution of the multispin system with the interaction Hamiltonian given by Eq. (2.10). Since the number of all the possible eigenvectors $\mathbf{g}_{l,N}(0)$ is given in terms of the binomial coefficients $\binom{N-1}{l}$ as $N\binom{N-1}{l}$, the expression for the N-spin FID becomes

$$\frac{G(t)}{Z}=\mathbf{g}_N^T(0)\,\exp_O\Bigg\{\sum_{n=1}^{\infty}(-i\chi)^n\sum_{i<j}^{N}[\mathbf{C}^{(ij)}]^n\times\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\times\langle F(\mathbf{r}(t_1))F(\mathbf{r}(t_2))\cdots F(\mathbf{r}(t_n))\rangle_c\Bigg\}\mathbf{g}_N(0)$$

$$=NO\Bigg\langle\exp_O\Bigg[-i\frac{3}{4}\chi\int_0^t dt'F(\mathbf{r}(t'))\Bigg]+\exp_O\Bigg[i\frac{3}{4}\chi\int_0^t dt'F(\mathbf{r}(t'))\Bigg]\Bigg\rangle^{N-1}. \quad (4.10)$$

As follows from Eq. (4.10), the averaged many-body FID is expressed in terms of a two-body signal when the motions of the spin pairs are stochastically independent. The two-body FID can be evaluated by the method of the stochastic Liouville equation.[3,5,19,20] In the thermodynamic limit, N, $V\to\infty$ (where V is the sample volume) Eq. (4.10) becomes (see Ref. 7 for details)

$$G(t)=G(0)\exp N\int_0^t\frac{dt'}{V}\frac{\partial g_2(t')}{\partial t'}. \quad (4.11)$$

Thus, the signal arising from collective interactions of N spins relaxes to its equilibrium much faster than the corresponding two-body signal $g_2(t)$, since on average any two spins spend most of the time away from each other when $V\to\infty$. That is, for nearly all times of interest (on the many-body time scale), it is sufficient just to know the short-time behavior of the two-body signal.

Plots of the many-body line shapes at different concentrations of spins are shown in Fig. 2. Calculations have been performed by using Eq. (4.11) as described in Ref. 7 for an ultraslow motional regime corresponding to the value of the relative translational diffusion coefficient of $D_T=10^{-4}\,\gamma^2\hbar/d$. The numbers of spins have been chosen to be $N=10^4$, 10^5, 10^6, and 10^7 and the ratio of the distance of maximum separation to the distance of minimal approach has been set to $r_{\max}/r_{\min}=100$. Convergence to the thermodynamic limit has been checked as described in Ref. 7. If the distance of minimal approach is chosen to be $r_{\min}\equiv d=5$ Å, the above values of N correspond to concentrations of spins C of: (a) 1.9×10^{19}, (b) 1.9×10^{20}, (c) 1.9×10^{21}, and (d) $1.9\times10^{22}\,\mathrm{cm}^{-3}$, respectively. As can be seen from Fig. 2, Eq. (4.11) describes a transition from Lorentzian line shapes corresponding to low (a) concentrations, to Gaussian line shapes corresponding to high (d) concentrations of spins. An intermediate regime [plots (b) and (c)] can also be seen. Fits of the calculated spectra to the Lorentzian [plots (a) and (b)] and Gaussian [plots (c) and (d)] functions are shown by dashed lines for comparison.

V. DIRECT-PRODUCT FORMALISM FOR CALCULATING THE EVOLUTION OF VARIOUS ORDERS OF COHERENCE FOR MULTIPLE PULSES

From the following formal equation for the evolution of the density matrix components in the eigenoperator representation, one can calculate motionally averaged signals corresponding to various orders of coherence in the presence of an intermediate pulse $\mathbf{X}$:

$$\mathbf{g}(t)=\langle e_O^{-i\mathbf{\Delta\Omega}(t-\tau)-i\chi\Sigma_{i_1<j_1}^N\mathbf{C}^{(i_1j_1)}\int_\tau^t dt_1F(r_{i_1j_1}(t_1))}\times\mathbf{X}e_O^{-i\mathbf{\Delta\Omega}\tau-i\chi\Sigma_{i_1<j_1}^N\mathbf{C}^{(i_1j_1)}\int_0^\tau dt_1F(r_{i_1j_1}(t_1))}\rangle\mathbf{g}(0), \quad (5.1)$$

where the diagonal coherence matrix $\mathbf{\Delta\Omega}$ treats the off-resonance effects. Its representation in the eigenoperator basis is given by Eq. (2.8), which can be rewritten as a sum of "dressed" direct-product structures by analogy with the C-matrices and the starting vector $\mathbf{g}(0)$,

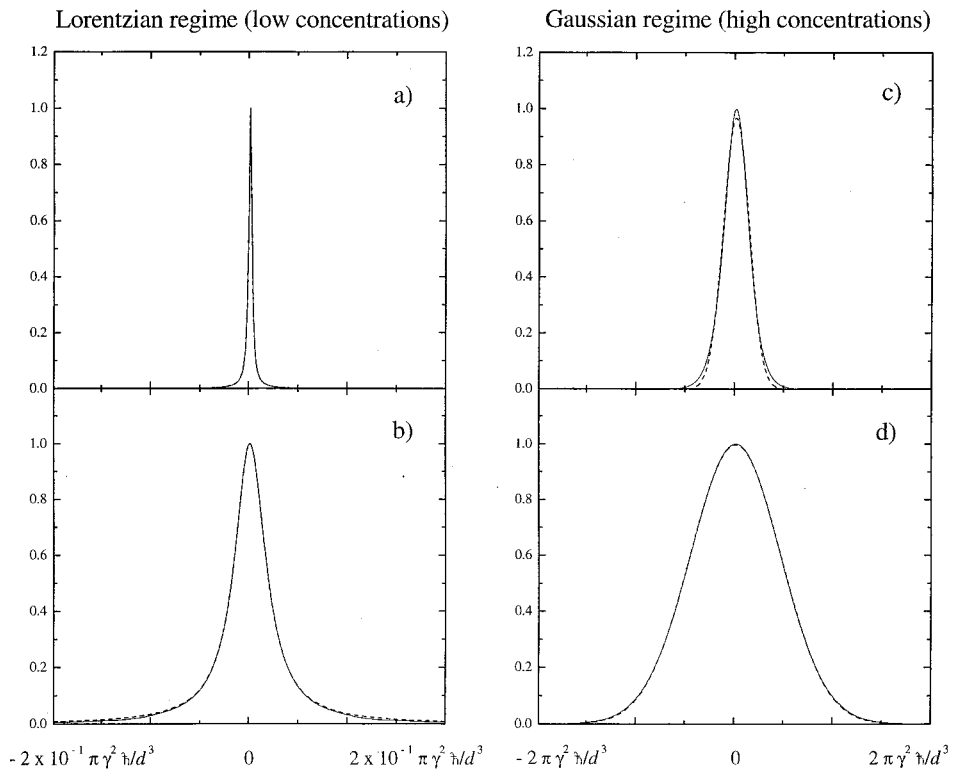

FIG. 2. Plots of the many-body line shapes at different concentrations of spins: (a) 1.9×10^{19}, (b) 1.9×10^{20}, (c) 1.9×10^{21}, and (d) $1.9\times10^{22}\ \mathrm{cm}^{-3}$, cf. the text. A transition from a Lorentzian regime [low concentrations, (a)] to a Gaussian regime [high concentrations, (d)] can be seen. An intermediate regime corresponds to plots (b) and (c). Dashed lines show fits to Lorentzian [plots (a) and (b)] and Gaussian [plots (c) and (d)] functions.

$$\mathbf{\Delta\Omega}=\sum_{i=0}^{N-1}\{\mathbf{E}\}^{i}\otimes\mathbf{\Delta\Omega}_{i+1}\otimes\{\mathbf{E}\}^{N-1-i}. \tag{5.2}$$

Here the offset matrix for the ith spin is given by

$$\mathbf{\Delta\Omega}_i=\Delta\omega_i\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}, \tag{5.3}$$

where $\Delta\omega_i=\omega_i-\omega_{\mathrm{rf}}$. Note that in the case of like spins, the C-matrices commute with the coherence matrices $\mathbf{\Delta\Omega}$, which can be checked directly by computing the commutator

$$[\mathbf{C}_2,\mathbf{E}\otimes\mathbf{\Delta\Omega}_i+\mathbf{\Delta\Omega}_i\otimes\mathbf{E}]=0. \tag{5.4}$$

The elements of the pulse propagator matrix $\mathbf{X}^T$ in the eigenoperator space are defined as

$$\begin{aligned}X_{\{\epsilon\}\{\epsilon'\}}&\equiv\mathrm{Tr}[E^{\dagger}_{\{\epsilon'\}}R(\theta)E_{\{\epsilon\}}R^{-1}(\theta)]\\&=\mathrm{Tr}[E_{\{\epsilon\}}R^{-1}(\theta)E^{\dagger}_{\{\epsilon'\}}R(\theta)].\end{aligned} \tag{5.5}$$

In the direct-product representation, the overall *nonselective* pulse propagator acts on each spin individually, and can be simply written as

$$\mathbf{X}_N=\mathbf{X}\otimes\mathbf{X}\otimes\mathbf{X}\otimes\cdots=\{\mathbf{X}\}^N. \tag{5.6}$$

Clearly, in the case of *selective* pulses the X-matrices corresponding to unaffected spins should be replaced by unit matrices $\mathbf{E}$. The pulse propagator $\mathbf{X}$ for individual spins for a $(\pi/2)_y$ pulse is given by

$$\mathbf{X}_y=\frac{1}{2}\begin{pmatrix}1&1&-1&-1\\-1&1&1&-1\\1&1&1&1\\-1&1&-1&1\end{pmatrix}, \tag{5.7}$$

and for a $(\pi/2)_x$ pulse

$$\mathbf{X}_x=\frac{1}{2}\begin{pmatrix}1&i&-i&1\\i&1&1&-i\\-i&1&1&i\\1&-i&i&1\end{pmatrix}. \tag{5.8}$$

Since the exchange terms are not affected by a pulse, $\mathbf{X}\mathbf{C}^{\mathrm{ex}(ij)}\mathbf{X}^{-1}=\mathbf{C}^{\mathrm{ex}(ij)}$, one may repeat the arguments of the previous section for the case of intermediate pulses. In the case of like spins one may, therefore, consider the truncated version of the dipolar Hamiltonian containing only the $I_z^{(i)}I_z^{(j)}$ terms, and subsequently replace the coupling constant χ by $3\chi/2$. We shall also consider the pure resonance case, $\Delta\omega=0$, as before. The eigenoperator representation of the truncated dipolar Hamiltonian superoperator matrix then simply becomes diagonal, and can be rewritten as

$$\begin{aligned}\mathbf{C}_2&=(I_z\otimes\mathbf{e})\otimes(I_z\otimes\mathbf{e})-(\mathbf{e}\otimes I_z)\otimes(\mathbf{e}\otimes I_z)\\&=\tfrac{1}{2}(\mathbf{A}\otimes\mathbf{B}+\mathbf{B}\otimes\mathbf{A}),\end{aligned} \tag{5.9}$$

where the auxiliary matrices $\mathbf{A}$ and $\mathbf{B}$ are given by

$$\mathbf{A}=\mathbf{A}_1-\mathbf{A}_2, \tag{5.10a}$$

$$\mathbf{A}_1\equiv\begin{pmatrix}1&&&\\&0&&\\&&0&\\&&&0\end{pmatrix},\quad \mathbf{A}_2\equiv\begin{pmatrix}0&&&\\&0&&\\&&0&\\&&&1\end{pmatrix},$$

$$\mathbf{B}=\mathbf{B}_1-\mathbf{B}_2, \tag{5.10b}$$

$$\mathbf{B}_1\equiv\begin{pmatrix}0&&&\\&1&&\\&&0&\\&&&0\end{pmatrix},\quad \mathbf{B}_2\equiv\begin{pmatrix}0&&&\\&0&&\\&&1&\\&&&0\end{pmatrix}.$$

In order to make use of the recurrence relation, Eq. (3.7), directly, let us consider a system containing $N+1$ identical spins instead of N. Since all the matrices are diagonal, they commute with each other, and the time-ordered matrix exponential for $N+1$ spins in Eq. (5.1) can be simply rewritten in terms of ordinary matrix exponentials as

$$\begin{aligned}&e_O^{-i\chi\Sigma_{i<j}^{N+1}\mathbf{C}^{(ij)}\int_0^t dt' F(r_{ij}(t'))}\\&\quad=\mathbf{E}\otimes e^{-i\chi\Sigma_{2\le i<j}^{N+1}\mathbf{C}^{(ij)}\int_0^t dt' F(\mathbf{r}_{ij}(t'))}\\&\qquad\times e^{-i\chi\Sigma_{m=1}^{N}\Pi_m(\mathbf{C}_2\otimes\{\mathbf{E}\}^{N-1})\Pi_m^{-1}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}.\end{aligned} \tag{5.11}$$

To compute the matrix exponential of the second term, we write explicitly the sum over the permutations, viz.,

$$\begin{aligned}&\sum_{m=1}^{N}\Pi_m(\mathbf{C}_2\otimes\{\mathbf{E}\}^{N-1})\Pi_m^{-1}\\&\quad=\tfrac{1}{2}(\mathbf{A}\otimes\mathbf{B}\otimes\{\mathbf{E}\}^{N-1}+\mathbf{A}\otimes\mathbf{E}\otimes\mathbf{B}\otimes\{\mathbf{E}\}^{N-2}+\cdots\\&\qquad+\mathbf{A}\otimes\{\mathbf{E}\}^{N-1}\otimes\mathbf{B}+\mathbf{B}\otimes\mathbf{A}\otimes\{\mathbf{E}\}^{N-1}\\&\qquad+\mathbf{B}\otimes\mathbf{E}\otimes\mathbf{A}\otimes\{\mathbf{E}\}^{N-2}+\cdots+\mathbf{B}\otimes\{\mathbf{E}\}^{N-1}\otimes\mathbf{A}).\end{aligned} \tag{5.12}$$

We then apply the following property of the matrix exponential of a dressed direct-product sum,[8]

$$\begin{aligned}&e^{\mathbf{A}\otimes\mathbf{E}\otimes\cdots\otimes\mathbf{E}+\mathbf{E}\otimes\mathbf{B}\otimes\cdots\otimes\mathbf{E}+\cdots+\mathbf{E}\otimes\mathbf{E}\otimes\cdots\otimes\mathbf{Z}}\\&\quad=e^{\mathbf{A}}\otimes e^{\mathbf{B}}\otimes\cdots\otimes e^{\mathbf{Z}},\end{aligned} \tag{5.13}$$

which is valid for any matrices $\mathbf{A},\mathbf{B},\ldots\mathbf{Z}$ of the same size as the unit matrix $\mathbf{E}$. The result is

$$\begin{aligned}&e^{-i\chi\Sigma_{m=1}^{N}\Pi_m(\mathbf{C}_2\otimes\{\mathbf{E}\}^{N-1})\Pi_m^{-1}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}\\&\quad=\mathbf{A}_1\prod_{m=1}^{N}\otimes e^{-i(\chi/2)\mathbf{B}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}\\&\qquad+\mathbf{A}_2\prod_{m=1}^{N}\otimes e^{+i(\chi/2)\mathbf{B}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}\\&\qquad+\mathbf{B}_1\prod_{m=1}^{N}\otimes e^{-i(\chi/2)\mathbf{A}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}\\&\qquad+\mathbf{B}_2\prod_{m=1}^{N}\otimes e^{+i(\chi/2)\mathbf{A}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}.\end{aligned} \tag{5.14}$$

From the recurrence relation, Eq. (3.4), and by using the above equation, one obtains a very important expression which describes evolution of the starting vector corresponding to the first-order (or single-quantum, $\mu=\pm1$) coherence,

$$\begin{aligned}\mathbf{g}^{(\pm1)}(t)&=e^{-i\chi\Sigma_{i<j}^{N}\mathbf{C}^{(ij)}\int_0^t dt' F(\mathbf{r}_{ij}(t'))}\mathbf{g}^{(\pm1)}(0)\\&\equiv\sum_{m=1}^{N}\mathbf{g}_m^{(\pm1)}(t)\\&=\sum_{m=1}^{N}(e^{\mp ik_{1m}(t)}\mathbf{i}_\alpha+e^{\pm ik_{1m}(t)}\mathbf{i}_\beta)\\&\quad\otimes\cdots\otimes(e^{\mp ik_{m-1m}(t)}\mathbf{i}_\alpha+e^{\pm ik_{m-1m}(t)}\mathbf{i}_\beta)\\&\quad\otimes\mathbf{i}_\pm\otimes(e^{\mp ik_{mm+1}(t)}\mathbf{i}_\alpha+e^{\pm ik_{mm+1}(t)}\mathbf{i}_\beta)\\&\quad\otimes\cdots\otimes(e^{\mp ik_{mN}(t)}\mathbf{i}_\alpha+e^{\pm ik_{mN}(t)}\mathbf{i}_\beta),\end{aligned} \tag{5.15}$$

where the functions $k_{ij}(t)$ are defined by

$$k_{ij}(t)\equiv\frac{\chi}{2}\int_0^t dt' F(\mathbf{r}_{ij}(t')), \tag{5.16}$$

and the summation in Eq. (5.15) is carried out for $i<j$. It is sufficient to verify Eq. (5.15) just for the first spin and then apply permutation symmetry arguments to obtain the remaining terms for the rest of the identical spins. For instance, the first exponential operator of Eq. (5.11) has no effect on the evolution of coherence of the first spin ($i=1$), $\mathbf{i}_+\otimes\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N$, and for the second exponential operator one has

$$\begin{aligned}&e^{-i\chi\Sigma_{m=1}^{N}\Pi_m(\mathbf{C}_2\otimes\{\mathbf{E}\}^{N-1})\Pi_m^{-1}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}\mathbf{i}_+\otimes\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N\\&\quad=\mathbf{A}_1\mathbf{i}_+\prod_{m=1}^{N}\otimes e^{-i(\chi/2)\mathbf{B}\int_0^t dt' F(\mathbf{r}_{1m+1}(t'))}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\\&\quad=\mathbf{i}_+\prod_{m=1}^{N}\otimes(e^{-ik_{1m+1}(t)}\mathbf{i}_\alpha+e^{+ik_{1m+1}(t)}\mathbf{i}_\beta),\end{aligned} \tag{5.17}$$

i.e., in agreement with the first term of Eq. (5.15).

Note that in the case of the truncated dipolar Hamiltonian the time evolution is contained only in the $\mathbf{i}_{\alpha,\beta}$ terms, which allows one to obtain the exact result, Eq. (5.15). If the motions of the spins are stochastically independent, the motional averaging of the direct products in Eq. (5.15) followed by projection onto the vector $\mathbf{g}^{(+1)T}(0)$ yields immediately the binomial result, Eq. (4.10), even without using cumulants.

Next, we apply an intermediate $(\pi/2)_y$ pulse (which corresponds to a standard solid-echo experiment) to see what happens to our N-spin system. The observed single-quantum coherence signal is given by

$$\frac{G(t)}{Z}=\mathbf{g}^{(+1)T}(0)\langle e^{-i\chi\Sigma_{i_1<j_1}^{N}\mathbf{C}^{(i_1j_1)}\int_{\tau}^{t}dt_1F(\mathbf{r}_{i_1j_1}(t_1))}\times\mathbf{X}e^{-i\chi\Sigma_{i_1<j_1}^{N}\mathbf{C}^{(i_1j_1)}\int_{0}^{\tau}dt_1F(\mathbf{r}_{i_1j_1}(t_1))}\rangle\mathbf{g}^{(+1)}(0)=\langle\mathbf{g}^{T}(t-\tau)\mathbf{X}\mathbf{g}(\tau)\rangle, \tag{5.18}$$

since the C-matrices are symmetric. To calculate $\mathbf{X}\mathbf{g}(\tau)$, we note that

$$\mathbf{X}_y\mathbf{i}_{\pm}=\tfrac{1}{2}(\mathbf{i}_{\pm}-\mathbf{i}_{\mp})-\tfrac{1}{2}(\mathbf{i}_{\alpha}-\mathbf{i}_{\beta}), \tag{5.19a}$$

$$\mathbf{X}_y(e^{-ik_{ij}(t)}\mathbf{i}_{\alpha}+e^{+ik_{ij}(t)}\mathbf{i}_{\beta})=\cos k_{ij}(t)(\mathbf{i}_{\alpha}+\mathbf{i}_{\beta})+i\sin k_{ij}(t)(\mathbf{i}_{+}+\mathbf{i}_{-}). \tag{5.19b}$$

As one can see, the intermediate $(\pi/2)_y$ pulse produces a whole variety of multiquantum coherences in the many-body system of interacting spins upon acting on $\mathbf{g}(\tau)$ which is given by Eq. (5.15) evaluated at $t=\tau$. If the motions of the spin pairs are stochastically independent then the averaging over $k_{ij}(t)$ yields the same values. Thus, it is sufficient to calculate the effect of the pulse just for the first spin and then multiply the intensity by N. After applying the pulse propagator to each subvector of Eq. (5.15) as given by Eqs. (5.19a) and (5.19b), followed by motional averaging and combining the similar terms together, the overall echo signal becomes

$$G(t)=\frac{qN}{2}[\langle\cos k(t-\tau)\cos k(\tau)\rangle^{N-1}+(N-1)\langle\sin k(t-\tau)\times\sin k(\tau)\rangle\langle\cos k(t-\tau)\rangle^{N-2}\langle\cos k(\tau)\rangle^{N-2}]. \tag{5.20}$$

Using the multiplication properties of the sine and cosine functions, the observed signal can be rewritten in terms of the two-body FID and echo as

$$G(t)=\frac{qN}{2}\left[2^{-(N-1)}\langle\mathrm{ECHO}|_0^t+\mathrm{FID}|_0^t\rangle^{N-1}+\frac{(N-1)}{2}\langle\mathrm{ECHO}|_0^t-\mathrm{FID}|_0^t\rangle\times\langle\mathrm{FID}|_{\tau}^{t}\rangle^{N-2}\langle\mathrm{FID}|_0^{\tau}\rangle^{N-2}\right], \tag{5.21}$$

where

$$\mathrm{FID}|_0^t\equiv\frac{e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}+e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}}{2}, \tag{5.22a}$$

$$\mathrm{ECHO}|_0^t\equiv\frac{e^{-i(\chi/2)\int_0^t dt's(t')F(\mathbf{r}(t'))}+e^{+i(\chi/2)\int_0^t dt's(t')F(\mathbf{r}(t'))}}{2}. \tag{5.22b}$$

Here the s-function is defined by: $s(t)=+1$, $t>\tau$, and $s(t)=-1$, $t<\tau$. It is noteworthy that when $N=2$ the observed signal consists entirely of the echo. As the number of spins increases, multiple quantum coherences produced in accordance with Eq. (5.19b) suppress the echo formation. This constitutes a well-known fact in solid-state NMR. At this point one has to compare Eq. (5.21) with Eq. (6.15) in Ref. 7. The latter has been derived for the case of a reduced basis operator set having $\mu=\pm1$, which implies neglecting any higher-order coherences produced by the second pulse.[21] By contrast, in deriving Eq. (5.21) we have used the full basis set as well as the full form of the pulse propagator, $\mathbf{X}$. For a very large number of spins, one can use the Markov averaging method[7,22,23] to obtain for $t>\tau$

$$G(t)=\frac{qN}{2}\left\{e^{(C/2)\int_0^t dt'\partial g_e(t')/\partial t'+\partial g_f(t')/\partial t'}+\frac{C}{2}[g_e(t)-g_f(t)]e^{C\int_0^t dt'\partial g_f(t')/\partial t'}\right\}=\frac{qN}{2}e^{C\int_0^t dt'\partial g_f(t')/\partial t'}\left\{e^{C/2[g_e(t)-g_f(t)]}+\frac{C}{2}[g_e(t)-g_f(t)]\right\}, \tag{5.23}$$

where $g_e(t)$ and $g_f(t)$ are the motionally averaged echo and FID for the two-spin problem, respectively, which can be evaluated by the method of stochastic Liouville equation as described in Ref. 20. In the solid-state limit, the averaging becomes just integration over volume,[14] and Eq. (5.23) at $t>\tau$ becomes

$$G(t)=\frac{qN}{2}e^{-t/T_2^*}\left(e^{(t-|t-2\tau)|/2T_2^*}+\frac{t-|t-2\tau|}{2T_2^*}\right). \tag{5.24}$$

At low enough concentrations of spins the relaxation time T_2^* is given by the classic Anderson formula,[24] $1/T_2^*=4\pi^2\gamma^2\hbar C/9\sqrt{3}$. At higher C a more complicated nonlinear behavior in time is found, which becomes Gaussian in the limit, cf. Fig. 2 and Appendix B of Paper II.[15] When $t=2\tau$ Eq. (5.24) becomes

$$G(2\tau)=\frac{qN}{2}\left(e^{-\tau/T_2^*}+\frac{\tau}{T_2^*}e^{-2\tau/T_2^*}\right). \tag{5.25}$$

The effect of echo suppression can be seen by comparing Eq. (5.25) with the result when generation of higher-order coherences is neglected, which predicts no decay at $t=2\tau$ when the translational diffusion coefficient, $D_T\to0$ for the solid echo, cf. Ref. 7. Note that the first part of Eq. (5.25) corresponds to just a single-exponential decay, but we do find the existence of a second term, which is seen to decay at twice the rate of the first term. However, the second part may not be always observed experimentally if $\tau\ll T_2^*$.

Plots of many-body spin-echoes for N identical spins of 1/2 calculated by using Eq. (5.23) at different values of the translational diffusion coefficient D_T are presented in Fig. 3 (solid lines). The evaluation of the averaged random-phase exponentials for the FID and echo components has been performed as described in Ref. 20. Even at the rigid limit ($D_T=10^{-6}\gamma^2\hbar/d$) there is no full echo refocusing, and at sufficiently long delay times no echo is expected at all. Note that the echo maximum does not occur at exactly $t=2\tau$. Increas-

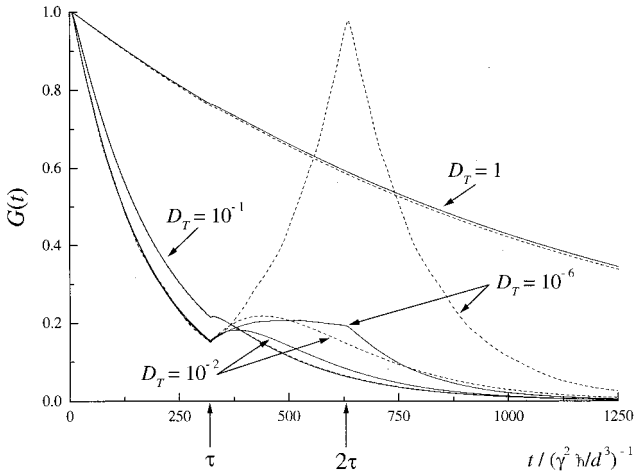

FIG. 3. Spin-echoes calculated at different values of the translational diffusion coefficient D_T (in units of $\gamma^2\hbar/d = 6.54\times10^{-6}$ cm^2/s for electrons if $r_{\min}=d=5$ Å) as shown in different panels. The number of spins and the ratio of the distance of maximum separation to the distance of minimal approach have been chosen to be $N=10^4$ and $r_{\max}/r_{\min}=100$, respectively, which corresponds to a concentration of spins of 1.9×10^{19} cm^{-3}. Even near the rigid limit ($D_T=10^{-6}\gamma^2\hbar/d$) there is no complete echo refocusing. Increasing the diffusion rate further decreases the echo and shifts its maximum to the left of $t=2\tau$. Dashed lines show the pure echo signal for comparison, i.e., $\exp C\int_0^t dt'[\partial g_e(t')/\partial t']$, cf. the text.

ing the diffusion rate not only further decreases the echo amplitude, but also shifts it towards the time τ when the pulse is applied. Dashed lines show the pure echo signal, i.e., the one considered in Ref. 7. In contrast to the more general expression, Eq. (5.23), the latter can be fully refocused at $t=2\tau$ in the rigid limit. Because of the technical limitations of the previous theory,[7] the earlier treatment did not include the formation of higher-order coherences after the second pulse. Instead, a truncated basis operator set (i.e., corresponding to $\mu=\pm1$) was used which was insufficient for a rigorous consideration of higher-order coherences that are formed after the refocusing pulse. (These results, shown as dashed lines in Fig. 3, are compared with the new results of this work.) However, when motions of the spins are sufficiently fast the two expressions become motionally averaged, which results in their similar behavior, cf. Fig. 3.

Figure 4 shows the echo behavior as a function of the delay time, τ calculated at various values of the diffusion coefficient, D_T. For electron spin-bearing molecules having the distance of minimal approach of $d=5$ Å, the range from $D_T=10^{-4}$ to 10^{-1} in units of $\gamma^2\hbar/d$ converts to from 6.5×10^{-10} to 6.5×10^{-7} cm^2 s^{-1}, which represents the range of translational diffusion rates in lipid membranes and other viscous solvents. The calculations for Fig. 4 have been performed for a concentration of spins 1.9×10^{19} cm^{-3} (32 mM). The time scale for each plot then corresponds to about 1.9 ns per unit time for electron spins. As can be seen, appreciable echo amplitudes are anticipated for τ's lying on a hundred-nanosecond time scale or less, which still should be measurable experimentally.[25] From Fig. 4 it is clear that a detailed comparison between experimental results and the theory presented here would be required to extract the experimental D_T. (Concentration-dependent studies would be also helpful.)

We now generalize Eq. (5.20) to the evolution of coherences of arbitrary order in a solid echo experiment. We write a higher-order coherence signal as, cf. Eq. (5.18),

$$\frac{G_\mu(t)}{Z} = \mathbf{g}^{(\mu)T}\langle e^{-i\chi\Sigma_{i_1<j_1}^N \mathbf{C}^{(i_1j_1)}\int_\tau^t dt_1 F(\mathbf{r}_{i_1j_1}(t_1))} \times \mathbf{X} e^{-i\chi\Sigma_{i_1<j_1}^N \mathbf{C}^{(i_1j_1)}\int_0^\tau dt_1 F(\mathbf{r}_{i_1j_1}(t_1))}\rangle \mathbf{g}^{(\pm1)}(0) = \langle \mathbf{g}^{(\mu)T}(t-\tau)\mathbf{X}\mathbf{g}^{(\pm1)}(\tau)\rangle. \quad (5.26)$$

Equation (5.26) is valid for any left-hand projection vector $\mathbf{g}^{(\mu)}$. Let us consider for simplicity those coherent density states $\mathbf{g}^{(\mu)}$ that contain μ subvectors $\mathbf{i}_+$, e.g., $\mathbf{g}^{(\mu)}=\{\mathbf{i}_+\}^\mu \otimes \{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^{N-\mu}$ plus all the permutations thereof. The signal corresponding to such multiple-quantum coherences can then

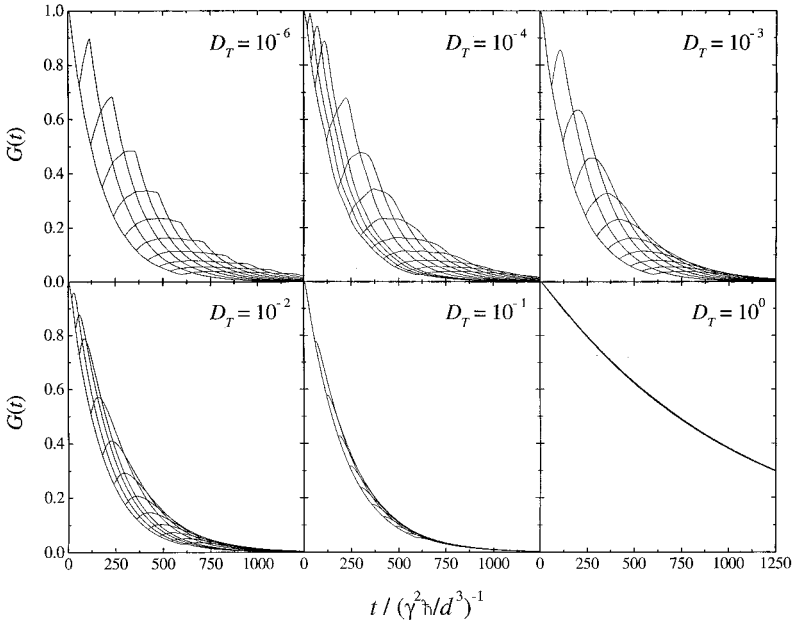

FIG. 4. Many-body spin-echoes calculated at different values of delay times τ [in units of $(\gamma^2\hbar/d^3)^{-1}=3.82\times10^{-10}$ s for electrons if $r_{\min}\equiv d=5$ Å] and the translational diffusion coefficient D_T (in units of $\gamma^2\hbar/d = 6.54\times10^{-6}$ cm^2/s) as shown in different panels. Longer delay times spread out the echo, whereas increasing the translational diffusion rate further decreases the echo amplitude.

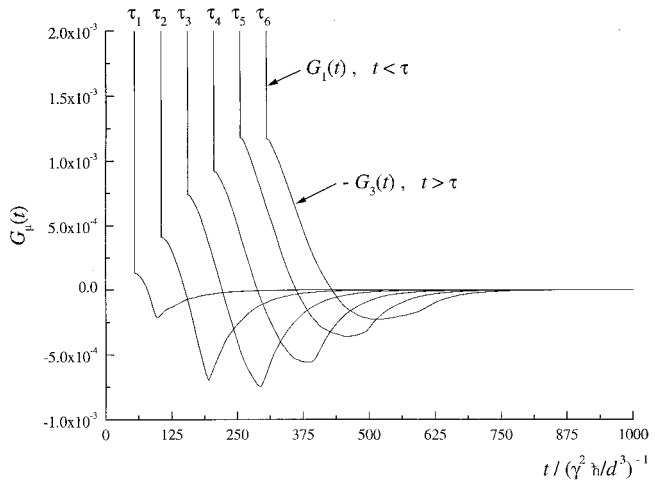

FIG. 5. Evolution of the triple-quantum coherence after the intermediate $(\pi/2)_y$ pulse in a solid-echo experiment after various pulse delay times, τ ($D_T=10^{-6}\gamma^2\hbar/d$, $C=1.9\times10^{19}\,\mathrm{cm}^{-3}$). The initial intensities of a triple-order coherence, $\mathbf{g}^{(3)}\equiv\Sigma_{\text{all permutations}}\{\mathbf{i}_+\}^3\otimes\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^{N-3}$ do not exceed 0.1% of the initial intensity of the first-order coherence, $G_1(0)=1$. However, due to a large variety of multiple-quantum coherences, the echo loss measured for the first-order coherence is still significant, cf. Fig. 3.

be obtained in exactly the same manner as has been done for the first-order coherence, Eq. (5.20). A somewhat tedious but straightforward calculation yields for $t>\tau$

$$\begin{aligned}\frac{G_\mu(t)}{Z}&=\langle\mathbf{g}^{(\mu)T}(t-\tau)\mathbf{X}\mathbf{g}^{(\pm1)}(\tau)\rangle\\&=i^{\mu-1}2^{N-\mu}\binom{N}{\mu}\Bigg[\mu\langle\sin\pm k(\tau)\rangle^{\mu-1}\\&\times\Bigg\langle\cos\sum_{m=1}^{\mu}k_m(t-\tau)\cos k_1(\tau)\Bigg\rangle^{N-\mu}+(N-\mu)\\&\times\Bigg\langle\sin\sum_{m=1}^{\mu}\pm k_m(t-\tau)\prod_{m=1}^{\mu}\sin\pm k_m(\tau)\Bigg\rangle\\&\times\Bigg\langle\cos\sum_{m=1}^{\mu}k_m(t-\tau)\Bigg\rangle^{N-\mu-1}\langle\cos k(\tau)\rangle^{N-\mu-1}\Bigg].\end{aligned}\tag{5.27}$$

Here we have introduced the index m (instead of the previous double index ij to simplify the expression) to designate stochastic dependences (correlations) between the spin pairs, which determines the way the averaging should be performed on products involving sine and cosine functions. For instance, when averaging the structures like $\langle\sin[k_1(t-\tau)+k_2(t-\tau)+k_3(t-\tau)]\sin k_1(\tau)\sin k_2(\tau)\sin k_3(\tau)\rangle$, the functions $k_1(\tau)$ and $k_1(t-\tau)$ must be correlated, and so on. The $G_\mu(t)$ for $\mu\neq1$ cannot be actually detected directly in a real experiment; an additional $\pi/2$ pulse is needed to convert them back to the single-quantum coherence.[26] Nevertheless, their evolution and initial intensities are still of interest. By comparing the expressions for k and $-k$, Eq. (5.27), it can be seen that only odd-order coherences survive after the second pulse due to the mutual cancelling of the even-order coherences arising from terms corresponding to $\mu=1$ and $\mu=-1$ in the starting (right-hand) vector, cf. Eq. (5.26). For instance, if $\mu=3$ one obtains from Eq. (5.27) in the thermodynamic limit, $N,V\to\infty$, but $N/V=C$

$$\begin{aligned}G_3(t)=-\frac{qN}{2}\frac{1}{2^2 3!}\Bigg\{&3C^2\langle\sin k(\tau)\rangle^2 e^{2C\int_\tau^t dt'\,\partial g_f(t')/\partial t'}\\&\times e^{C/2\int_0^t dt'\,\partial g_e(t')/\partial t'+\partial g_f(t')/\partial t'}\\&+\left(\frac{C}{2}\right)^3[3(c_E-c_F)(s_E-s_F)^2-(c_E-C_F)^3]\\&\times e^{3C\int_\tau^t dt'\,\partial g_f(t')/\partial t'}e^{C\int_0^\tau dt'\,\partial g_f(t')/\partial t'}\Bigg\},\end{aligned}\tag{5.28}$$

where

$$\begin{aligned}c_E&\equiv\langle\cos[k(t-\tau)-k(\tau)]\rangle'=\langle\mathrm{ECHO}|_0^t\rangle',\\c_F&\equiv\langle\cos[k(t-\tau)+k(\tau)]\rangle'=\langle\mathrm{FID}|_0^t\rangle',\\s_E&\equiv\langle\sin[k(t-\tau)-k(\tau)]\rangle',\\s_F&\equiv\langle\sin[k(t-\tau)+k(\tau)]\rangle'.\end{aligned}\tag{5.29}$$

In performing the above averaging in the thermodynamic limit we have used the following property of the Markov method

$$\begin{aligned}&[\tfrac{1}{2}\langle e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle^\mu+\tfrac{1}{2}\langle e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle^\mu]^N\\&=\Bigg\{1-\mu\frac{C}{N}\Bigg\langle1-\frac{1}{2}e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\\&\quad-\frac{1}{2}e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\Bigg\rangle'+\frac{\mu(\mu-1)}{4}\left(\frac{C}{N}\right)^2\\&\quad\times[\langle1-e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle'^2\\&\quad+\langle1-e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle'^2]-\cdots\Bigg\}^N\\&\to\exp-\mu C\langle1-\tfrac{1}{2}e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\\&\quad-\tfrac{1}{2}e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle',\end{aligned}\tag{5.30}$$

where the prime means taking the averaging over the unnormalized equilibrium probability distribution, cf. Ref. 7 for details. Thus, the decay of a multiple quantum coherence is proportional to its order, μ. Higher powers of $\mu C/N$ have no effect as $N\to\infty$. As one can see from Eqs. (5.28) and (5.29), in the case of triple coherences there are now sine terms involved, but they are also directly related to the motionally averaged exponentials that can be evaluated by solving the stochastic Liouville equation for the dipolar problem.[20]

Plots of the evolution of the triple-quantum coherence calculated from Eq. (5.28) are shown in Fig. 5 as a function of pulse delay time, τ. Because of the presence of dispersive sine terms in Eq. (5.28), the signal amplitude corresponding to $\mu=3$ can be negative. As one can see from the inset, the intensities of one given triple quantum coherence do not exceed 0.1% of the single-quantum coherence [all plots are normalized so that $G_1(0)=1$]. However, due to a very large

variety of multiple-quantum coherences, together they result in a significant loss of the echo amplitude measured for the first-order coherence. For instance, there are other coherences produced in a solid-echo pulse sequence, such as $\mathbf{g}^{(\mu,\kappa)}=\{\mathbf{i}_+\}^{\mu}\otimes\{\mathbf{i}_+\otimes\mathbf{i}_-\}^{\kappa}\otimes\{\mathbf{i}_\alpha\pm\mathbf{i}_\beta\}^{N-\mu-2\kappa}$ (plus all the permutations thereof) which have not been considered. However, the calculation of the evolution of such coherences is still possible, and represents a straightforward generalization of the theory presented herein.

VI. INSTANTANEOUS DIFFUSION IN ORDINARY ECHO EXPERIMENTS

To further investigate the nature of the echo loss in many-spin experiments, let us consider a collection of N_A spins of type A interacting with N_B spins of type B. We are interested in what will happen if only N_A spins are selectively flipped by an intermediate π-pulse. The evolution of spin-density states before the pulse is still described by Eq. (5.15) with $N=N_A+N_B$. The pulse propagator can be compactly written in this case as

$$\mathbf{X}_N=\{\mathbf{X}\}^{N_A}\otimes\{\mathbf{E}\}^{N_B}, \tag{6.1}$$

from which the choice of a numbering scheme for spins A and B becomes clear. For a π_x pulse, the matrix $\mathbf{X}$ is given by

$$\mathbf{X}_{(\pi)_x}=\begin{pmatrix} & & & 1\\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix}. \tag{6.2}$$

It is noteworthy that in the eigenoperator space the role of the matrix $\mathbf{X}$ is simply to interchange $\mathbf{i}_+$ with $\mathbf{i}_-$ and $\mathbf{i}_\alpha$ with $\mathbf{i}_\beta$. With this in mind and using Eqs. (5.1), (5.15), and (6.1), the absolute value of the nonvanishing projection of the ordinary echo signal $G_A(t)$ measured for spins A can be written as

$$\begin{aligned}\frac{|G_A(t)|}{Z}&=\langle\mathbf{g}^{(+1)T}(t-\tau)\mathbf{X}_N\mathbf{g}^{(-1)}(\tau)\rangle\\ &=\sum_{m=1}^{N_A}\langle\mathbf{g}_{m,A}^{(+1)T}(t-\tau)\{\mathbf{X}\}^{N_A}\mathbf{g}_{m,A}^{(-1)}(\tau)\rangle\\ &\quad\times\langle\mathbf{g}_{m,B}^{(0)T}(t-\tau)\mathbf{g}_{m,B}^{(0)*}(\tau)\rangle\end{aligned} \tag{6.3}$$

(since a direct product of any two complex numbers is a number itself). In the above expression we broke up total spin-density vectors into the first-order coherence parts corresponding to spins A and the remaining (zero-order coherence) parts for spins B, cf. Eq. (5.15). As can be seen from Eq. (6.3), there will be no refocusing of $A-A$ interactions, since $\{\mathbf{X}\}^{N_A}\mathbf{g}_{m,A}^{(-1)}(\tau)=\mathbf{g}_{m,A}^{(+1)}(\tau)$; whereas $A-B$ interactions get refocused since the left-hand and right-hand side vectors corresponding to spins B are related by complex conjugation, cf. Eqs. (5.15) and (6.3). Carrying out the necessary vector–vector multiplications involving the Kronecker-product algebra, we find that $G_A(t)$ consists of a product of two terms

$$\begin{aligned}\frac{|G_A(t)|}{Z}&=N_A\langle e^{-i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\\ &\quad+e^{+i(\chi/2)\int_0^t dt'F(\mathbf{r}(t'))}\rangle^{N_A-1}\langle e^{-i(\chi/2)\int_0^t dt's(t')F(\mathbf{r}(t'))}\\ &\quad+e^{+i(\chi/2)\int_0^t dt's(t')F(\mathbf{r}(t'))}\rangle^{N_B},\end{aligned} \tag{6.4}$$

where stochastic independence of the motions has been assumed. Thus, the ordinary echo consists of the product of a decaying FID term corresponding to $A-A$ interactions, and an echo-refocusing term corresponding to $A-B$ interactions. In the solid-state thermodynamic limit, application of the Markov method and integration over volume yields from Eq. (6.4), cf. Refs. 7 and 14,

$$|G_A(t)|=\frac{qN_A}{2}e^{-t/T_2^{*(AA)}}e^{-|t-2\tau|/T_2^{*(AB)}}, \tag{6.5}$$

where $1/T_2^{*(AA)}=4\pi^2\gamma_A^2\hbar C_A/9\sqrt{3}$, $1/T_2^{*(AB)}=4\pi^2\gamma_A\times\gamma_B\hbar C_B/9\sqrt{3}$. The first exponential terms represents the well-known effect of echo suppression referred to as instantaneous diffusion in solid-state ESR. Letting $t=2\tau$ we find that Eq. (6.5) corresponds exactly to the classical formula for instantaneous diffusion[13,23,24] developed previously in a more *ad hoc* fashion. Here we have proved it rigorously by using the direct-product formalism for the case of the truncated dipolar Hamiltonian. As can be seen from Eq. (6.5), $A-A$ interactions suppress the echo arising from $A-B$ interactions. It is worthwhile to emphasize that the nature of signal loss in an ordinary echo experiment is different from that for the solid echo considered in the previous section, Eq. (5.21). In the former case it is due to the fact that interactions amongst like spins cannot be refocused; whereas in the latter case the echo loss is due to the generation of multiple quantum coherences produced after the intermediate $(\pi/2)_y$ pulse.

VII. CONCLUSIONS

We have considered herein a new approach to the solution of the density-matrix equation for a multispin system based on a direct-product formalism. Hamiltonian supermatrices have been introduced based on the Frobenius trace metric defined in the eigenoperator space of the unperturbed Zeeman–Hamiltonian superoperator. Algebraic properties of the supermatrices allow for a convenient direct (or Kronecker) product factorization, which makes the present approach particularly useful for the case of many-spin problems. The superoperator approach makes it possible to obtain a solution even when the interaction Hamiltonian is time-dependent, thus explicitly incorporating spin relaxation into the theory. When the motions of the spins are stochastically independent, compact solutions can be obtained for the FID and echo signals due to the permutation symmetries and simple eigenvector properties of the superoperator matrices. The motional averaging of the matrix-exponential forms can be performed by the method of the stochastic Liouville equation (see Ref. 20, and Paper II[15] for details). This enables one to take into account time correlations of all orders

and, therefore, calculate motional effects of arbitrary time scale.

The exponential forms of the superoperator matrices can be evaluated exactly for the case of the truncated diagonal dipolar Hamiltonian, i.e., containing the terms $I_z^{(i)}I_z^{(j)}$ only. However, the additional exchange terms [i.e., $\mathbf{I}^{(i)}\mathbf{I}^{(j)}$] have been shown to have no effect (apart from the factor of 3/4 instead of 1/2 in the coupling constant) on the FID and echoes of like spins engaged in *stochastically independent motions*. This is a generalization of the result of the Anderson statistical model for dilute solids. It is due also to the fact that the exchange terms yield antisymmetric combinations of the spin-density states, which mutually cancel each other because of the permutation symmetry of the problem. When the difference in Larmor frequencies becomes large, thus suppressing the effects of the $I_{\pm}^{(i)}I_{\mp}^{(j)}$ terms, only the first (diagonal) part of the spin Hamiltonian of Eq. (2.6) is significant, and this just introduces a simple 2/3 scaling factor, cf. Eqs. (2.6) and (4.2).[27] In both cases, the FID decay will be predominantly governed by the $I_z^{(i)}I_z^{(j)}$ terms of the dipolar Hamiltonian. In Paper II we deal with a case where the $I_{\pm}^{(i)}I_{\mp}^{(j)}$ terms are treated for a crystalline lattice, wherein no assumption of stochastic independence is made.

The results presented herein can be extended to the existence of structure in the viscous or solid media to take into account interactions with other molecules in the sample. More specifically, the effects of other molecules can be included in the form of a structure factor describing the pair-correlation function in a mean-field approach.[28] This would affect the form of the diffusion operator in the stochastic-Liouville equation used for the averaging of spin transitions modulated by the dipolar interaction, while still being consistent with our assumption of stochastic independence of the motions of the spin-bearing molecules.

Previous results[7] have been rederived more efficiently and more elegantly for the FID and solid echo for a many-body system of identical spins of 1/2. Moreover, a more rigorous treatment of the many-body solid-echo, which was not possible by using the previous framework,[7] has been accomplished in the present paper. It has been found that the echo maximum does not occur at exactly twice the time of the pulse, and shifts towards earlier times. Generation of higher-order coherences after the second pulse greatly suppresses the echo formation in a multiple-spin system, and there is no complete echo refocusing even at the rigid limit. Nevertheless, the results presented here can be used to extract the diffusion coefficient, D_T from detailed comparisons with experiment.

It has been shown that in the thermodynamic limit the relaxation rate of a multiple-quantum coherence is proportional to its order, μ. The results also indicate that in the thermodynamic limit, i.e., at very large number of spins and sample volume, only the short-time behavior on the two-body time scale determines the relaxation of multiple-spin states to their equilibrium.

The well-known phenomenon of instantaneous diffusion in an ordinary echo experiment has been studied here from first principles (i.e., from calculating the evolution of spin-density states), and the effect of motional averaging has been included. In contrast to the solid echo pulse sequence, the echo maximum occurs here near $t=2\tau$, and the echo loss is due to the fact that dipolar interactions amongst like spins cannot be refocused. Thus, a clear distinction between the nature of the loss of refocusing in the solid and ordinary echoes has been made in the present work.

The formalism presented herein may find its use in modern NMR and ESR many-body problems such as Quantum Computing[10] and biophysical studies of membranes and proteins.[29] The expression for solid-state spin echoes can be of interest for measuring translational diffusion rates in viscous media such as glasses, liquid crystals, and membranes. The recursive nature of the direct-product factorization and the relatively simple matrix-vector multiplications involved (as opposed to the conventional matrix transformations) makes the present method convenient for computer implementations in the case of more complicated problems.

ACKNOWLEDGMENTS

The authors would like to thank Professor Jean Jeener for very useful comments on the manuscript. This work was supported by NIH and NSF grants.

[1] C. N. Banwell and H. Primas, Mol. Phys. **6**, 225 (1963).
[2] J. H. Freed, J. Chem. Phys. **49**, 376 (1968).
[3] J. H. Freed, in *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), pp. 165–191.
[4] J. Jeener, in *Adv. Magn. Reson.*, Vol. 10, edited by J. S. Waugh (Academic, New York, 1982), pp. 2–51.
[5] D. J. Schneider and J. H. Freed, Adv. Chem. Phys. **73**, 387 (1989).
[6] S. A. Smith, W. E. Palke, and J. T. Gerig, J. Magn. Reson., Ser. A **106**, 57 (1994).
[7] A. A. Nevzorov and J. H. Freed, J. Chem. Phys. **112**, 1425 (2000).
[8] W. H. Steeb, *Matrix Calculus and Kronecker Product with Applications and C++ Programs* (World Scientific, Singapore, 1997).
[9] S. Lee, W. Richter, S. Vathyam, and W. S. Warren, J. Chem. Phys. **105**, 874 (1996).
[10] Z. L. Mádi, R. Brüschweiler, and R. R. Ernst, J. Chem. Phys. **109**, 10603 (1998).
[11] J. Jeener, A. Vlassenbroek, and P. Broekaert, J. Chem. Phys. **103**, 1309 (1995).
[12] R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).
[13] J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).
[14] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).
[15] A. A. Nevzorov and J. H. Freed, J. Chem. Phys. **115**, 2416 (2001), following paper.
[16] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, Oxford, 1987).
[17] J. M. Ortega, *Matrix Theory. A Second Course* (Plenum, New York, 1987).
[18] G. Bodenhausen, H. Kogler, and R. R. Ernst, J. Magn. Reson. **58**, 370 (1984).
[19] R. Kubo, J. Phys. Soc. Jpn. **26**, 1 (1969).
[20] A. A. Nevzorov and J. H. Freed, J. Chem. Phys. **112**, 1413 (2000).
[21] It has been stated in Ref. 7 that stochastic independence of spin motions averages out higher-order coherences, which is incorrect. Thus, Eq. (6.15) of Ref. 7 should be regarded as approximately valid when a special pulse sequence is used which suppresses higher-order coherences (e.g., magic echoes).
[22] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[23] K. M. Salikhov and Y. D. Tsvetkov, in *Time Domain Electron Spin Resonance*, edited by L. Kevan and R. N. Schwartz (Wiley, New York, 1979), pp. 231–277.
[24] W. B. Mims, *Electron Paramagnetic Resonance* (Plenum, New York, 1972).
[25] J. H. Freed, Annu. Rev. Phys. Chem. **51**, 655 (2000).

[26] C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer-Verlag, Heidelberg, 1990).

[27] In the case of an admixture of spins A having a concentration of C_A interacting with spins A' with a concentration $C_{A'}$, one may generalize Eq. (4.11) in the case of nonselective excitation to: $G_A(t) \approx (qN_A/2)\exp[C_A \int_0^t dt'[\partial g_f^{(AA)}(t')/\partial t'] + C_{A'} \int_0^t dt'[\partial g_f^{(AA')}(t')/\partial t']]$, where the coupling constant corresponding to the AA' interactions is related to that of the AA interactions by: $\chi^{(AA')} = 2/3\chi^{(AA)}$. Furthermore, neglecting the presumably small second (linear in concentration) term in Eq. (5.23) [cf. discussion after Eq. (5.25)], one may generalize Eq. (5.23) in a similar way:

$$G_A(t) \approx \frac{qN_A}{2} \exp\left\{ \frac{C_A}{2} \int_0^t dt' \left[\frac{\partial g_f^{(AA)}(t')}{\partial t'} + \frac{\partial g_e^{(AA)}(t')}{\partial t'} \right] + \frac{C_{A'}}{2} \int_0^t dt' \left[\frac{\partial g_f^{(AA')}(t')}{\partial t'} + \frac{\partial g_e^{(AA')}(t')}{\partial t'} \right] \right\}.$$

The appropriate expression for $G_{A'}(t)$ is obtained by permuting A and A'.

[28] L. P. Hwang and J. H. Freed, J. Chem. Phys. **63**, 4017 (1975).

[29] P. L. Stewart, R. Tycko, and S. J. Opella, J. Chem. Soc., Faraday Trans. 1 **84**, 3803 (1988).