A many-body analysis of the effects of the matrix protons and their diffusional motion on electron spin resonance line shapes and electron spin echoes

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

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The method for treating the evolution of the density matrix developed in the accompanying paper for many-spin systems is applied here for calculating magnetic resonance signals of a spin A interacting with a bath of N identical spins B. Spins B are assumed to have much smaller gyromagnetic ratios than the spin A (e.g., the former are nuclear spins, I and the latter is an electron spin, S). The experimentally observed quadratic dependence of the spin-echo envelope decay on concentration and time is explained from considering the dipolar coupling of spin A to all the B spins in the presence of B–B dipolar interactions. It is shown that the spin-echo envelope decay in the rigid limit is due to the interaction of the A spin with the coherent many-body states of the coupled spins B via the nuclear flip-flop terms $I_{\pm}I_{\mp}$, which becomes a dissipative mechanism in the thermodynamic limit. This represents a more rigorous analysis than simplified models based on an incoherent version of ''spin diffusion,'' and it leads to good quantitative agreement with experiment. Moreover, this analysis represents a unified description of both the modulation and decay of the A-spin echoes. Spin echoes and line shapes for the A–B_N systems are also calculated for finite motions which randomize the B spins. Even for very slow motions (modeled as translational diffusion) an effective mechanism for spin-echo envelope decay is generated, which readily overtakes the coherent mechanism in importance. The intensity distribution for the forbidden components in the A-spin line shape resulting from multiquantum transitions of the B spins caused by the pseudosecular interaction terms $S_zI_{\pm}$, is calculated. In the rigid limit it is found to behave like a Poisson distribution. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1382817]

I. INTRODUCTION

In the present paper we investigate the relaxation of a single spin A having a large gyromagnetic ratio (e.g., an electron) interacting with a bath of N identical spins having much lower gyromagnetic ratios, B (e.g., protons). We further develop the direct-product superoperator method proposed in the previous paper[1] for calculating magnetic resonance signals in many-body systems. In our earlier work,[1–3] a system of like spins was considered. Due to the high symmetry of the problem, it was sufficient to consider only the secular part of the dipolar Hamiltonian. The final expressions were reduced to motionally averaged exponential functions which effectively correspond to two-body interactions taken to the Nth power, provided that the motions are stochastically independent. In the case of unlike spins, additional terms in the dipolar Hamiltonian usually need to be considered, including induced nuclear spin-flip transitions of the bath spins and off-resonance effects. This may make obtaining closed-form analytical solutions no longer possible. Therefore, in order to make the problem tractable, additional simplifications may be necessary.

In much of this work we focus on the solid-state limit, which is still of practical importance. As is well-known in ESR, in the solid-state limit the matrix protons cause: (i) Electron-spin echo envelope modulation (ESEEM), and (ii) an irreversible decay of the electron spin echo amplitude. The ESEEM theory is well developed.[4,5] A treatment of the echo envelope decay was proposed nearly three decades ago.[6–8] It was based on the theory of Klauder and Anderson[9] of a random-field modulation at the electron caused by random flip-flops of the neighboring pairs of proton spins due to nuclear ''spin diffusion.'' However, the proton–proton interactions are coherent, so the simplification of introducing the random flip–flops is only a crude approximation. A more accurate approach requires that all the protons, as well as the electron, be considered together as a single many-body quantum system. It is expected that the electron interactions with this coherent ''bath'' of protons should have a dissipative effect in the thermodynamic limit, i.e., in the limit of an infinitely large bath. This should yield a decay of the electron-spin echo amplitude versus time (i.e., a T_2-type decay). However, there are subtle aspects of such a complicated picture requiring detailed examination. Our many-body analysis is shown to compare very favorably with ESR experiments in frozen systems.

In the nuclear magnetic resonance (NMR) case, a theory for the nuclear spin-lattice relaxation (T_1) in solids in the presence of paramagnetic impurities was developed years ago.[10–12] It is based on modeling the transfer of magnetization between the nuclear spins as diffusive in nature, and it is this process that has been termed spin diffusion. Recently,

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

however, the coherent nature of this phenomenon has been recognized. Brüschweiler and Ernst[13,14] have considered linear chains of spins of 1/2 from first principles (i.e., as a single quantum system) with a dipolar Hamiltonian involving the spin-flipping terms, i.e., $I_{\pm}^{(i)}I_{\mp}^{(j)}$ for nuclei i and j. In the solid-state limit, this leads to a nonergodic quasiequilibrium behavior of the longitudinal magnetization of the spins (i.e., when the final state of the system cannot be described by a single temperature); whereas the spin-diffusion *Ansatz* would predict ergodic behavior. In the present paper, however, we discuss the free-induction decay (FID) and spin echoes of an electron spin embedded in a bath of interacting nuclear spins, and this necessarily directs our attention to T_2-type processes.

In addition, we shall investigate what happens when the temperature is raised and motions are introduced. This is a matter of great importance for ESR experiments in viscous media for which no useful theory has existed up to the present time.[5–8] In this analysis we assume random motions, corresponding to the assumption of stochastic independence of the motions that we have previously utilized,[1–3] so positional correlations amongst the matrix protons are lost. We first show rigorously that any effects of the spin diffusion of the matrix protons (i.e., the $B-B$ interactions) vanish in the fast motional limit, as expected. Then for slow to intermediate translational diffusion rates, we calculate the magnetic-resonance signals from the A (electron) spin interacting with B spins (protons) by solving a system of coupled stochastic Liouville equations, as described in Appendix A. In Appendix B, an analytic expression for the distribution of intensities corresponding to the forbidden ESR transitions, which are multiquantum in nuclear spins, is obtained in the solid-state limit.

II. DIRECT-PRODUCT FORMULATION OF THE PROBLEM IN THE SUPEROPERATOR REPRESENTATION

The dipolar interaction Hamiltonian in the rotating frame for an $A-B_N$ system is chosen as

$$H_{A-B}^{(1i)}=\chi_0 F_0(\mathbf{r}_{1i})S_z I_z^{(i)}+\chi_1[F_-(\mathbf{r}_{1i})S_z I_+^{(i)} + F_+(\mathbf{r}_{1i})S_z I_-^{(i)}], \tag{2.1a}$$

$$H_{B-B}^{(ij)}=\chi F_0(\mathbf{r}_{ij})[I_z^{(i)}I_z^{(j)}-\tfrac{1}{4}(I_+^{(i)}I_-^{(j)}+I_-^{(i)}I_+^{(j)})]. \tag{2.1b}$$

As usual, we neglect in Eq. (2.1a) the electron spin-flip terms, since these transitions are of too high energy to be important except for very fast motions.[15] The pseudosecular $S_zI_\pm$ terms are in general significant,[15] leading to electron-spin echo envelope modulation,[4,5] and are therefore, retained.

Spin A is chosen here to be the first spin, and the coupling constants are given by: $\chi_0\equiv\sqrt{(16\pi/5)}\gamma_A\gamma_B\hbar$, $\chi_1\equiv\sqrt{(6\pi/5)}\gamma_A\gamma_B\hbar$, $\chi\equiv\sqrt{(16\pi/5)}\gamma_B^2\hbar$. The functions that depend on the distance $\mathbf{r}$ between the spins are expressed in terms of the spherical harmonics as

$$F_0(\mathbf{r})=\frac{Y_0^{(2)}(\theta,\phi)}{r^3},\quad F_-(\mathbf{r})=\frac{Y_1^{(2)*}(\theta,\phi)}{r^3},\quad F_+(\mathbf{r})=\frac{Y_1^{(2)}(\theta,\phi)}{r^3}. \tag{2.2}$$

The equation of motion for the spin-density vector $\mathbf{g}(t)$ (the density matrix equation in the eigenoperator representation), cf. Eq. (2.7) of Paper I[1] now becomes

$$\frac{\partial\mathbf{g}(t)}{\partial t}=-i(\mathbf{\Delta\Omega}+\mathbf{H}^x)\mathbf{g}(t). \tag{2.3}$$

The $(N+1)$-body frequency offset (coherence) matrix is given by the representation of the Zeeman Hamiltonian superoperator in the eigenoperator space, cf. Eq. (5.2) of Paper I,[1] viz.,

$$\mathbf{\Delta\Omega}=\mathbf{\Delta\Omega}_A\otimes\{\mathbf{E}\}^N+\mathbf{E}\otimes\mathbf{\Delta\Omega}_B^{(N)}=\mathbf{E}\otimes\mathbf{\Delta\Omega}_B^{(N)}, \tag{2.4}$$

since spin A is assumed to be on resonance, $\Delta\Omega_A=0$. The N-body offset matrix $\Delta\Omega_B^{(N)}$ for spins B is also given by an equation of the type of Eq. (5.2) of Paper I. The representation of the many-body interaction Hamiltonian superoperator in the eigenoperator basis becomes [here we can use the recursion relation, Eq. (3.7) of Paper I,[1] directly]

$$\mathbf{H}^x=\mathbf{E}\otimes\sum_{2\leqslant i<j}^{N+1}\chi\mathbf{C}^{(ij)}F(\mathbf{r}_{ij})+\sum_{m=1}^{N}\Pi_m[\chi_0\mathbf{C}_0F_0(\mathbf{r}_{1m+1}) +\chi_1\mathbf{D}_+F_-(\mathbf{r}_{1m+1})+\chi_1\mathbf{D}_-F_+(\mathbf{r}_{1m+1})] \otimes\{\mathbf{E}\}^{N-1}\Pi_m^{-1}.$$

The first term on the right-hand side of Eq. (2.5) corresponds to the interactions of B spins within the bath, and is given by Eqs. (3.16) and (3.17) of Paper I.[1] The second term corresponds to the interactions of spin A with the B spins of the bath. Note that the superoperator formulation, Eq. (2.3) allows $\mathbf{H}^x$ to be time-dependent, where the time dependence may be implicitly contained in the classical variables $\mathbf{r}$. The two-spin C-matrix describing the secular terms of the interaction of spin A with spins B (corresponding to the S_zI_z terms) is fully diagonal, and can be factorized as

$$\mathbf{C_0}=\frac{1}{2}\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}\otimes\begin{pmatrix}0&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&0\end{pmatrix} +\frac{1}{2}\begin{pmatrix}0&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&0\end{pmatrix}\otimes\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix} \equiv\tfrac{1}{2}(\Sigma'\otimes\Sigma+\Sigma\otimes\Sigma'). \tag{2.6}$$

The two-spin D-matrices (corresponding to the $S_zI_\pm$ terms) are related by the matrix transpose, $\mathbf{D}_-=\mathbf{D}_+^T$, and can be also factorized into two parts

$$\mathbf{D}_+ = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \end{pmatrix} \equiv \tfrac{1}{2}(\Sigma' \otimes \Delta + \Sigma \otimes \Delta'). \tag{2.7}$$

The matrices of Eqs. (2.6) and (2.7) can be obtained by a laborious calculation of the commutation relations of the S_zI_z and $S_zI_\pm$ terms with the eigenoperators $S_\epsilon I_\epsilon$, $\epsilon = +,\alpha,\beta,-$. Note that any mixed inner product of the two matrix terms is zero in both Eqs. (2.6) and (2.7).

In the absence of motions, the formal solution of Eq. (2.3) can be written as

$$\mathbf{g}(t) = e^{-i(\boldsymbol{\Delta\Omega}+\mathbf{H}^x)t}\mathbf{g}(0). \tag{2.8}$$

Since $\gamma_B \ll \gamma_A$ the B-spins are way off resonance, so they are not rotated by the radio frequency (rf) pulses. This allows one to write the first-order coherence starting vector including both $\mu=+1$ and $\mu=-1$ components simply as

$$\mathbf{g}(0) = \mathbf{g}_+(0) - \mathbf{g}_-(0) = (\mathbf{i}_+ - \mathbf{i}_-) \otimes \{\mathbf{i}_\alpha + \mathbf{i}_\beta\}^N. \tag{2.9}$$

This corresponds to having the entire initial magnetization in the X–Y plane concentrated at spin A, or $\rho(0) \propto S_y$. The reader is reminded here that the curly brackets denote a direct product repeated N times. Using the properties $\Sigma'\mathbf{i}_\pm = \pm\mathbf{i}_\pm$ and $\Sigma\mathbf{i}_\pm = \mathbf{0}$, Eq. (2.8) can be simplified to

$$\mathbf{g}(t) = \mathbf{i}_+ \otimes e^{-i(\mathbf{H}^x_{A-B}+\mathbf{H}^x_{B-B})t}\{\mathbf{i}_\alpha + \mathbf{i}_\beta\}^N - \mathbf{i}_- \otimes e^{-i(\tilde{\mathbf{H}}^x_{A-B}+\mathbf{H}^x_{B-B})t}\{\mathbf{i}_\alpha + \mathbf{i}_\beta\}^N. \tag{2.10}$$

Here the reduced Hamiltonian supermatrices are given by

$$\mathbf{H}^x_{A-B} = \sum_{m=1}^{N} \{\mathbf{E}\}^{m-1} \otimes \left[\Delta\Omega_B + \frac{\chi_0}{2}\Sigma F_0(\mathbf{r}_{1m+1}) + \frac{\chi_1}{2}\Delta F_-(\mathbf{r}_{1m+1}) + \frac{\chi_1}{2}\Delta^{\mathbf{T}}F_+(\mathbf{r}_{1m+1})\right] \otimes \{\mathbf{E}\}^{N-m}, \tag{2.11a}$$

$$\tilde{\mathbf{H}}^x_{A-B} = \sum_{m=1}^{N} \{\mathbf{E}\}^{m-1} \otimes \left[\Delta\Omega_B - \frac{\chi_0}{2}\Sigma F_0(\mathbf{r}_{1m+1}) - \frac{\chi_1}{2}\Delta F_-(\mathbf{r}_{1m+1}) - \frac{\chi_1}{2}\Delta^{\mathbf{T}}F_+(\mathbf{r}_{1m+1})\right] \otimes \{\mathbf{E}\}^{N-m}, \tag{2.11b}$$

$$\mathbf{H}^x_{B-B} = \chi \sum_{2 \leq i < j}^{N+1} \mathbf{C}^{(ij)} F_0(\mathbf{r}_{ij}), \tag{2.11c}$$

where the tilde simply means changing the sign everywhere except for the nuclear Zeeman term, $\Delta\Omega_B$. Thus, zero projections of the starting vector reduce the number of matrices that need to be considered for calculating the evolution of the magnetization for spin A.

III. SPIN-ECHO ENVELOPE DECAY DUE TO THE MATRIX PROTONS IN A–B_N SYSTEMS

The results presented in this paper can be regarded as a many-body formulation of the electron spin-echo envelope modulation (ESEEM) theory[5] for spins of 1/2, where the Larmor frequencies of the B spins, Ω_B result in a modulation of the echo amplitude. We shall see that the interactions among the B spins yield an additional loss of the echo amplitude, apart from the motional contribution which is discussed in Sec. V.

To calculate the effect of the intermediate π_x pulse in a Hahn-echo experiment, we use Eq. (5.1) of Paper I in the absence of motions

$$\frac{G(t)}{Z} = \mathbf{g}_+(0)^{\mathrm{T}} e^{-i(\boldsymbol{\Delta\Omega}+\mathbf{H}^x)(t-\tau)} \mathbf{X}_{(\pi)_x} e^{-i(\boldsymbol{\Delta\Omega}+\mathbf{H}^x)(\tau)} \mathbf{g}(0). \tag{3.1}$$

The prefactor Z arises from the high-temperature approximation of the equilibrium density operator and is given by $Z \equiv 2^{-(N+1)}\hbar\Omega_A/kT \equiv 2^{-(N+1)}q$. The X-matrix corresponding to π_x pulse, acts on spin A only, viz.,

$$\mathbf{X}_{(\pi)_x} = \begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix} \otimes \{\mathbf{E}\}^N. \tag{3.2}$$

Thus, the role of the X-matrix in this case is simply to swap the $\mu=+1$ component with the $\mu=-1$ component. Using Eqs. (2.10) and (3.1) one obtains for the echo signal

$$\frac{|G(t)|}{Z} = \{\mathbf{i}^{\mathrm{T}}_\alpha + \mathbf{i}^{\mathrm{T}}_\beta\}^N e^{-i(\mathbf{H}^x_{A-B}+\mathbf{H}^x_{B-B})(t-\tau)} \times e^{-i(\mathbf{H}^x_{A-B}+\mathbf{H}^x_{B-B})\tau}\{\mathbf{i}_\alpha + \mathbf{i}_\beta\}^N. \tag{3.3}$$

In general, one needs to consider all couplings of the B–B interactions to the A–B interactions. Since the matrices in Eq. (3.3) do not commute, a rigorous calculation of all couplings amongst $\mathbf{H}^x_{A-B}$ and $\mathbf{H}^x_{B-B}$ represents a formidable (if not impossible) task. In general, Eq. (3.3) can be rewritten as a product of the exponential functions of the matrices involved and a commutator expansion containing powers of τ. However, since $\chi \ll \chi_0, \chi_1$ (since $\gamma_B \ll \gamma_A$), it is expected that τ^3 and higher-order commutator terms involving higher powers of $\mathbf{H}^x_{B-B}$ will start having an appreciable effect only at long enough times at which the signal has decayed almost completely due to the lower-order terms. Thus, the spin relaxation of an electron interacting with N protons should be mainly determined by the leading τ and τ^2 terms. It will be illustrated below that this leads to an expansion in powers of γ_B/γ_A. We may, therefore, restrict ourselves to the first order in $\mathbf{H}^x_{B-B}$ and write that

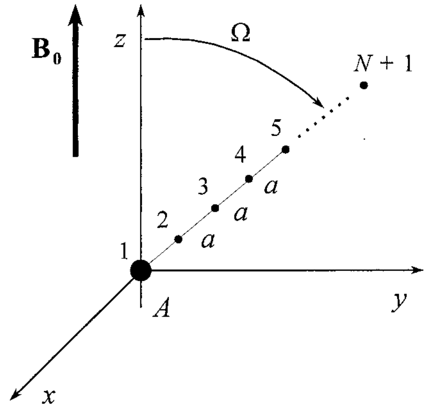

FIG. 1. A spherically symmetric radial model describing interactions of an electron spin with the matrix protons separated by a distance a in a rigid lattice. Only nearest-neighbor interactions between the protons are considered, whereas the electron is interacting with all the protons.

$$
\begin{aligned}
&e^{-i(\mathbf{H}^x_{A-B}+\mathbf{H}^x_{B-B})t}\\
&\quad= e^{-i\mathbf{H}^x_{A-B}t} e_{\mathrm{O}}^{-i\int_0^t dt' \exp(i\mathbf{H}^x_{A-B}t')\mathbf{H}^x_{B-B}\exp(-i\mathbf{H}^x_{A-B}t')}\\
&\quad\approx e^{-i\mathbf{H}^x_{A-B}t} e^{[\mathbf{H}^x_{A-B},\mathbf{H}^x_{B-B}]t^2/2} e^{-i\mathbf{H}^x_{B-B}t},
\end{aligned}
\tag{3.4}
$$

where the symbol "O" stands for the Dyson time-ordering. The approximate equality follows from the Zassenhaus formula,[16] which is used to expand the operator in the exponential in a series of commutators, keeping only the lowest order powers of t.

We can then rewrite Eq. (3.3) as

$$
\begin{aligned}
\frac{G(t)}{Z} \approx &\{\mathbf{i}^{\mathrm{T}}_{\alpha}+\mathbf{i}^{\mathrm{T}}_{\beta}\}^N e^{-i\mathbf{H}^x_{B-B}(t-\tau)} e^{[\mathbf{H}^x_{A-B},\mathbf{H}^x_{B-B}](t-\tau)^2/2}\\
&\times e^{-i\mathbf{H}^x_{A-B}(t-\tau)} e^{-i\tilde{\mathbf{H}}^x_{A-B}\tau} e^{-[\tilde{\mathbf{H}}^x_{A-B},\mathbf{H}^x_{B-B}]\tau^2/2}\\
&\times e^{-i\mathbf{H}^x_{B-B}\tau}\{\mathbf{i}_{\alpha}+\mathbf{i}_{\beta}\}^N.
\end{aligned}
\tag{3.5}
$$

The bath term, $\mathbf{H}^x_{B-B}$ has no effect on the starting vector since $\mathbf{C}^{(ij)}\{\mathbf{i}_{\alpha}+\mathbf{i}_{\beta}\}^N=0$, cf. Eq. (4.4) of Paper I,[1] and the commutator with the tilde term coincides with that without the tilde term except for the opposite sign, cf. Eqs. (2.11a) and (2.11b). At $t=2\tau$ we obtain the following simplified expression for the echo envelope decay (neglecting for now the off-resonance effects of Ω_B that lead to the relatively small spin-echo envelope modulation):

$$
\begin{aligned}
\frac{G(2\tau)}{Z} \approx &\{\mathbf{i}^{\mathrm{T}}_{\alpha}+\mathbf{i}^{\mathrm{T}}_{\beta}\}^N e^{[\mathbf{H}^x_{A-B},\mathbf{H}^x_{B-B}]\tau^2/2} e^{-i\mathbf{H}^x_{A-B}\tau} e^{-i\tilde{\mathbf{H}}^x_{A-B}\tau}\\
&\times e^{[\mathbf{H}^x_{A-B},\mathbf{H}^x_{B-B}]\tau^2/2}\{\mathbf{i}_{\alpha}+\mathbf{i}_{\beta}\}^N\\
\approx &\{\mathbf{i}^{\mathrm{T}}_{\alpha}+\mathbf{i}^{\mathrm{T}}_{\beta}\}^N e^{[\mathbf{H}^x_{A-B},\mathbf{H}^x_{B-B}]\tau^2}\{\mathbf{i}_{\alpha}+\mathbf{i}_{\beta}\}^N.
\end{aligned}
\tag{3.6}
$$

Thus, the coupling between the $\mathbf{H}^x_{A-B}$ and $\mathbf{H}^x_{B-B}$ terms yields an additional quadratic dependence in τ, whereas the $\exp[-i\mathbf{H}^x_{A-B}\tau]\exp[-i\tilde{\mathbf{H}}^x_{A-B}\tau]$ term yields the ESEEM effects which will be calculated in Sec. VI.

Let us consider a simple radial model (effectively one-dimensional) including all interactions of spin A with the B spins, and only nearest-neighbor interactions between the B spins, Fig. 1. We will generalize it shortly to three dimensions for the case of spherical symmetry. We shall retain only the diagonal part of the dipolar Hamiltonian describing the A–B interactions (i.e., containing the matrix Σ only). As will be seen later, the pseudosecular $S_z I^{(i)}_{\pm}$ terms of the Hamiltonian do not appreciably contribute to the echo amplitude in the rigid limit, causing relatively small amplitude modulation effects in the thermodynamic limit. Clearly, the secular part of $\mathbf{H}^x_{B-B}$ corresponding to the $I^{(i)}_z I^{(j)}_z$ terms of the dipolar Hamiltonian commutes with the secular part of $\mathbf{H}^x_{A-B}$ [or $\mathbf{H}^{x(\mathrm{sec})}_{A-B}$], corresponding to the $S_z I^{(i)}_{\pm}$ terms, and thus has no effect. Furthermore, $\mathbf{H}^x_{B-B}$ commutes with the offset matrices containing $\Delta\Omega_B$, cf. Eq. (5.4) of Paper I.[1] The flip–flop part of $\mathbf{H}^x_{B-B}$ [or $\mathbf{H}^{x(FF)}_{B-B}$], corresponding to the $I^{(i)}_{\pm} I^{(j)}_{\mp}$ terms, is given by, cf. Eq. (3.17) of Paper I,[1]

$$
\begin{aligned}
\mathbf{H}^{x(FF)}_{B-B} = -\frac{\chi}{4}\sum_{m=1}^{N-1} &F_0(\mathbf{r}_{m+1m+2})\{\mathbf{E}\}^{m-1}\otimes[(I_+\otimes\mathbf{e})\\
&\otimes(I_-\otimes\mathbf{e})-(\mathbf{e}\otimes I_+)\otimes(\mathbf{e}\otimes I_-)]\otimes\{\mathbf{E}\}^{N-m-1}\\
&+F_0(\mathbf{r}_{m+1m+2})\{\mathbf{E}\}^{m-1}\otimes[(I_-\otimes\mathbf{e})\\
&\otimes(I_+\otimes\mathbf{e})-(\mathbf{e}\otimes I_-)\otimes(\mathbf{e}\otimes I_+)]\otimes\{\mathbf{E}\}^{N-m-1}.
\end{aligned}
\tag{3.7}
$$

With Eq. (3.7) we can calculate the commutator of Eq. (3.6),

$$
\begin{aligned}
[\mathbf{H}^{x(\mathrm{sec})}_{A-B},\mathbf{H}^{x(FF)}_{B-B}] = \frac{\chi\chi_0}{2}\sum_{m=1}^{N-1} &F_0(\mathbf{r}_{m+1m+2})\{\mathbf{E}\}^{m-1}\\
&\otimes[F_0(\mathbf{r}_{1m+1})\Sigma\otimes\mathbf{E}+F_0(\mathbf{r}_{1m+2})\\
&\times\mathbf{E}\otimes\boldsymbol{\Sigma},\mathbf{C}_2]\otimes\{\mathbf{E}\}^{N-m-1}\\
= -\frac{\chi\chi_0}{8}\sum_{m=1}^{N-1} &F_0(\mathbf{r}_{m+1m+2})[F_0(\mathbf{r}_{1m+1})\\
&-F_0(\mathbf{r}_{1m+2})]\{\mathbf{E}\}^{m-1}\otimes[(I_+\otimes\mathbf{e})\\
&\otimes(I_-\otimes\mathbf{e})+(\mathbf{e}\otimes I_+)\otimes(\mathbf{e}\otimes I_-)\\
&-(I_-\otimes\mathbf{e})\otimes(I_+\otimes\mathbf{e})-(\mathbf{e}\otimes I_-)\otimes(\mathbf{e}\otimes I_+)]\\
&\otimes\{\mathbf{E}\}^{N-m-1}.
\end{aligned}
\tag{3.8}
$$

Here the index m is used to number the spins along the radius, cf. Fig. 1, and the matrix $\mathbf{C}_2$ corresponds to two-body interactions between the B spins. In deriving Eq. (3.8) the following commutation relations have been taken into account:

$$
\begin{aligned}
&[\Sigma,(I_+\otimes\mathbf{e})]=(I_+\otimes\mathbf{e}),\\
&[\Sigma,(\mathbf{e}\otimes I_+)]=-(\mathbf{e}\otimes I_+),\\
&[\Sigma,(I_-\otimes\mathbf{e})]=-(I_-\otimes\mathbf{e}),\\
&[\Sigma,(\mathbf{e}\otimes I_-)]=(\mathbf{e}\otimes I_-).
\end{aligned}
\tag{3.9}
$$

We then use the following property of the matrix exponential:

$$\{\mathbf{i}_\alpha^T+\mathbf{i}_\beta^T\}^2 e^{\chi\chi_0\tau^2/2F_0(\mathbf{r}_{m+1m+2})[F_0(\mathbf{r}_{1m+1})\boldsymbol{\Sigma}\otimes\mathbf{E}+F_0(\mathbf{r}_{1m+2})\mathbf{E}\otimes\boldsymbol{\Sigma},\mathbf{C}_2]}$$

$$\times\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^2=4\cos^2\left\{\frac{\chi\chi_0\tau^2}{8}F_0(\mathbf{r}_{m+1m+2})\times[F_0(\mathbf{r}_{1m+1})-F_0(\mathbf{r}_{1m+2})]\right\}, \tag{3.10}$$

which can be quickly obtained by using *Mathematica*, for example. The noncommutativity of the matrices in Eq. (3.8) would yield orders higher than χ (and, consequently, higher orders in τ^2), and thus can be neglected for $N\to\infty$ (infinite bath), cf. the discussion before Eq. (3.4). This makes it possible to generalize Eq. (3.10) to

$$\{\mathbf{i}_\alpha^{\mathrm{T}}+\mathbf{i}_\beta^{\mathrm{T}}\}^N e^{-[\mathbf{H}_{A-B}^{x(\mathrm{sec})},\mathbf{H}_{B-B}^{x(FF)}]\tau^2}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N$$
$$\underset{N\to\infty}{\to} 2^{N+1}\prod_{m=1}^{N-1}\cos^2\left\{\frac{\chi\chi_0\tau^2}{8}F_0(\mathbf{r}_{B-B})\times[F_0(\mathbf{r}_{1m+1})-F_0(\mathbf{r}_{1m+2})]\right\}$$
$$\approx 2^{N+1}\prod_{m=1}^{N-1}\cos^2\left\{\frac{3}{8}\frac{\chi\chi_0\tau^2}{a^2}\frac{[Y_0^{(2)}(\Omega)]^2}{r_{m+1}^4}\right\}, \tag{3.11}$$

the proof of which is straightforward, but is too long to be reproduced here. At $N\to\infty$ we take the natural logarithm of Eq. (3.11), replace the summation by integration over $\mathbf{r}_{1m}$, and then generalize the integration to three dimensions according to the following scheme:

$$\sum_{m=1}^{N-1}\overset{1-D}{\to}\int\frac{dr}{a}\overset{3-D}{\to}\int\frac{d\Omega}{4\pi}\int_0^\infty W(r)\frac{dr}{a}=\int\frac{d\Omega}{4\pi}\int_0^\infty\frac{2r^3dr}{3a^4}, \tag{3.12}$$

where a is the distance between the spins in the rigid lattice. The weighting function $W(r)=\frac{2}{3}(r/a)^3$ takes into account the fact that as the distance r increases, the number of possible pathways through which the magnetization can travel, also increases.[17] As a crude estimate, one can assume that the number of new pathways created for a given r is proportional to the number of spins $dN(r)$ confined within the spherical volume element $r^2drd\Omega$ with $r=ma$ and $dr=a$, i.e., $dN(r)\propto m^2d\Omega$. In the case of three-site flips in a cubic lattice, the proportionality factor is equal to 2 (the existing paths plus two new paths for each spin). The weighting function $W(r)$ in Eq. (3.12) can then be easily obtained from its recursion relation, $W(r_m)d\Omega=W(r_{m-1})d\Omega+2dN(r_m)$.

One can then write an expression for the spin-echo amplitude decay due to the irreversible loss of $x-y$ magnetization of the A-spin due to its coupling to the infinite bath of matrix protons

$$G(2\tau)\propto\exp\int\frac{d\Omega}{4\pi}\int_0^\infty\frac{2r^3dr}{3a^4}\times\ln\cos^2\left\{\frac{3}{8}\frac{\chi\chi_0\tau^2}{a^2}\frac{[Y_0^{(2)}(\Omega)]^2}{r^4}\right\}$$
$$=\exp-\frac{\pi}{20}\frac{\gamma_B}{\gamma_A}(C\gamma_A\gamma_B\hbar\tau)^2, \tag{3.13}$$

where $C\equiv a^{-3}$ is the number density of protons in the solid matrix. In obtaining Eq. (3.13) we have used the orthonormality property of the spherical harmonics and the following integral[18]

$$\int_0^\infty\frac{\ln\cos^2 bx}{x^2}dx=-\pi|b|. \tag{3.14}$$

Note that Eq. (3.13) contains the prefactor $\gamma_B/\gamma_A\ll1$, which yields a time scale separation between the faster decay of the many-body electron FID which is determined by just the $\exp(-i\mathbf{H}_{A-B}^x t)$ term [e.g., Eq. (3.3) with the role of the π-pulse ignored], and the slower decay of the electron spin-echo envelope due to proton spin diffusion. Thus, the assumption leading to Eq. (3.4) appears justified *a posteriori*.

At this point it is worthwhile to compare our result to that of Milov *et al.*[7] Their theory is simply based on a random modulation of the local field at the electron due to random flips of pairs of the proton spins that are distant from the electron. Rewriting their Eq. (14) in the form of our Eq. (3.13) one has

$$G(2\tau)\propto\exp-1.4\frac{\gamma_B}{\gamma_A}(C\gamma_A\gamma_B\hbar\tau)^{7/4}. \tag{3.15}$$

Milov *et al.* show that in fact a square-law dependence of the echo decay is experimentally observed in both C and τ, and they obtain the relatively close power of 7/4 given by Eq. (3.15). In our treatment the square-law dependence follows naturally from considering the coupling of the $S_zI_z^{(i)}$ terms to the $I_\pm^{(i)}I_\mp^{(j)}$ nuclear flip–flop terms treated up to the first-order commutators. Assuming the dependence $G(2\tau)\propto\exp(-AC^2\tau^2)$, Milov *et al.* report a factor of $A=7\times10^{-35}\,\mathrm{cm^6/s^2}$ measured from fitting the experimental data. Substituting the numerical values for gyromagnetic ratios of electron and proton in Eq. (3.13) we get $A=5.9\times10^{-35}\,\mathrm{cm^6/s^2}$, which is a rather good agreement with experiment. It should be noted that we did not arbitrarily introduce any random process for the frequency modulation. Instead, we have obtained the final result, Eq. (3.13) directly by solving the equation for the many-spin density operator, which emphasizes the coherent nature of spin diffusion.

IV. VANISHING EFFECT OF THE CORRELATIONS AMONG THE MATRIX PROTONS ON THE ELECTRON FID IN THE REDFIELD LIMIT

A noteworthy limiting case is the well-known Redfield, or fast motional limit. To solve the equation for the evolution of the density states, we go to the interaction-picture representation,

$$\mathbf{g}(t)=e^{-i\Delta\Omega t}\hat{\mathbf{g}}(t), \tag{4.1}$$

for which the formal solution averaged over motions becomes

$$\hat{\mathbf{g}}(t)=\left\langle \exp_O - i\int_0^t dt' e^{i\Delta\Omega t'}\mathbf{H}^x(t')e^{-i\Delta\Omega t'}\right\rangle \mathbf{g}(0). \quad (4.2)$$

The exponential operator can be simplified greatly by using the formula for the exponential function of a sum over ''dressed'' direct-product structures,[19]

$$e^{\mathbf{A}\otimes\mathbf{E}\otimes\cdots\otimes\mathbf{E}+\mathbf{E}\otimes\mathbf{B}\otimes\cdots\otimes\mathbf{E}+\cdots+\mathbf{E}\otimes\mathbf{E}\otimes\cdots\otimes\mathbf{Z}}=e^{\mathbf{A}}\otimes e^{\mathbf{B}}\otimes\cdots\otimes e^{\mathbf{Z}}, \quad (4.3)$$

which yields

$$e^{-i\Delta\Omega t}=e^{-i\Delta\Omega_A t}\otimes e^{-i\Delta\Omega_B t}\otimes e^{-i\Delta\Omega_B t}\otimes e^{-i\Delta\Omega_B t}\cdots$$
$$=\mathbf{E}\otimes\{e^{-i\Delta\Omega_B t}\}^N. \quad (4.4)$$

The frequency-offset matrix exponentials, $\exp(-i\Delta\Omega_B t)$ commute with the C-matrices (since they are both diagonal). For the D-matrices we use the following property:

$$\mathbf{D}_{\pm}(\mathbf{E}\otimes e^{-i\Delta\Omega_B t})=(\mathbf{E}\otimes e^{-i\Delta\Omega_B t})\mathbf{D}_{\pm}e^{\pm i\Omega_B t}, \quad (4.5)$$

i.e., they commute to within a scalar multiplier, which can be checked directly by multiplying the matrices given by Eq. (5.3) of Paper I and Eq. (2.7) of the present paper.

Next, by using Eqs. (2.5) and (4.5) we write the solution, Eq. (4.2), as

$$\hat{\mathbf{g}}(t)=\Bigg\langle \exp_O\Bigg\{\mathbf{E}\otimes - i\chi\sum_{2\leq i<j}^{N+1}\mathbf{C}^{(ij)}\int_0^t dt' F(\mathbf{r}(t'))+\sum_{m=1}^{N}\Pi_m\Bigg[-i\chi_0\mathbf{C}_0\int_0^t dt' F_0(\mathbf{r}(t'))$$
$$-i\chi_1\mathbf{D}_+\int_0^t dt' F_-(\mathbf{r}(t'))e^{i\Omega_B t'}-i\chi_1\mathbf{D}_-\int_0^t dt' F_+(\mathbf{r}(t'))e^{-i\Omega_B t'}\otimes\{\mathbf{E}\}^{N-1}\Bigg]\Pi_m^{-1}\Bigg\}\Bigg\rangle\mathbf{g}(0). \quad (4.6)$$

Equation (4.6) can be further rewritten in terms of generalized cumulant averages by taking into account stochastic independence of the motions of the $A-B$ spin pairs,

$$\hat{\mathbf{g}}(t)=\exp_O\Bigg\{O\sum_{n=1}^{\infty}\mathbf{E}\otimes\Bigg\langle\sum_{2\leq i<j}^{N+1}-i\chi\mathbf{C}^{(ij)}\int_0^t dt' F(\mathbf{r}_{ij}(t'))\Bigg\rangle_c^n+\sum_{m=1}^{N}\Pi_m\Bigg\langle -i\chi_0\mathbf{C}_0\int_0^t dt' F_0(\mathbf{r}(t'))$$
$$-i\chi_1\mathbf{D}_+\int_0^t dt' F_-(\mathbf{r}(t'))e^{i\Omega_B t'}-i\chi_1\mathbf{D}_-\int_0^t dt' F_+(\mathbf{r}(t'))e^{-i\Omega_B t'}\Bigg\rangle_c^n\otimes\{\mathbf{E}\}^{N-1}\Pi_m^{-1}\Bigg\}\mathbf{g}(0). \quad (4.7)$$

Here we have introduced the following shorthand notation for cumulant time-ordered averages:

$$O\left\langle\int_0^t dt' f(\mathbf{r};t')\right\rangle_c^n\equiv\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\langle f(\mathbf{r};t_1)f(\mathbf{r};t_2)\cdots f(\mathbf{r};t_n)\rangle_c, \quad (4.8)$$

where the time dependence in the function $f(\mathbf{r};t)$ may be both explicit and implicit.

For sufficiently fast motions, we can truncate the cumulant expansion of the motionally averaged exponential superoperator at the second order in a manner analogous to Refs. 3 and 20, which yields

$$\frac{G(t)}{Z}=\{\mathbf{i}_\alpha^{\mathrm{T}}+\mathbf{i}_\beta^{\mathrm{T}}\}^N\exp_O-\int_0^t dt_1\int_0^{t_1}dt_2\chi^2\sum_{2\leq i<j}^{N+1}[\mathbf{C}^{(ij)}]^2\langle F_0(\mathbf{r}(t_1))F_0(\mathbf{r}(t_2))\rangle_c+\sum_{m=1}^{N}\{\mathbf{E}\}^{m-1}\otimes\Bigg\{\frac{\chi_0^2}{4}\Sigma^2\langle F_0(\mathbf{r}(t_1))F_0(\mathbf{r}(t_2))\rangle_c$$
$$+\frac{\chi_1^2}{4}[\Delta\Delta^{\mathrm{T}}\langle F_-(\mathbf{r}(t_1))F_+(\mathbf{r}(t_2))\rangle_c e^{i\Omega_B(t_1-t_2)}+\Delta^{\mathrm{T}}\Delta\langle F_+(\mathbf{r}(t_1))F_-(\mathbf{r}(t_2))\rangle_c e^{-i\Omega_B(t_1-t_2)}]\Bigg\}\otimes\{\mathbf{E}\}^{N-m}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N. \quad (4.9)$$

[We have assumed that $\langle F_{0,\pm1}(\mathbf{r})\rangle=0$.] It can be shown by direct calculation that $\mathbf{i}_\alpha+\mathbf{i}_\beta$ is an eigenvector of the matrices Σ^2, $\Delta\Delta^{\mathrm{T}}$, and $\Delta^{\mathrm{T}}\Delta$, with eigenvalues of 1, 2, and 2, respectively. Thus, there will be no effect of the bath term [$\mathbf{H}_{B-B}^x$ of Eq. (2.1b)] since $\mathbf{C}^{(ij)}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N=0$. This yields the Redfield-limit FID corresponding to the Hamiltonian given by Eqs. (2.1a) and (2.1b),

$$G(t)=G(0)\exp\left\{-N\frac{2\pi}{5}\gamma_A^2\gamma_B^2\hbar^2\left[J_0(0)+\frac{3}{2}J_1(\Omega_B)\right]t\right\}, \quad (4.10)$$

where $J_m(\omega)$ are the spectral densities of motion defined as

$$J_m(\omega)\equiv 2\int_0^\infty d\tau\cos(\omega\tau)\langle F_m^*(\mathbf{r}(\tau))F_m(\mathbf{r}(0))\rangle_c. \quad (4.11)$$

Equation (4.10) means that even if the $S_zI_\pm$ pseudosecular terms are included, the FID decay rate is still linear with respect to the number of B-spins, N and there is no effect of the $B-B$ interactions.

V. ELECTRON SPIN FID'S AND ECHO ENVELOPE MODULATION IN THE PRESENCE OF TRANSLATIONAL DIFFUSION

By using Eq. (4.7), we can rewrite the motionally averaged expression for the FID signal in terms of generalized cumulants as

$$\frac{G(t)}{Z}=\{\mathbf{i}_\alpha^{\mathrm{T}}+\mathbf{i}_\beta^{\mathrm{T}}\}^N \exp_O\left\{ O\sum_{n=1}^{\infty}\left\langle \sum_{2\leqslant i<j}^{N+1} -i\chi\mathbf{C}^{(ij)}\int_0^t dt'F(\mathbf{r}_{ij}(t'))\right\rangle_c^n + \sum_{m=1}^{N}\{\mathbf{E}\}^{m-1}\otimes\left\langle -i\int_0^t dt'\mathbf{B}(\Omega_B,t')\right\rangle_c^n\otimes\{\mathbf{E}\}^{N-m}\right\}\{\mathbf{i}_\alpha+\mathbf{i}_\beta\}^N. \quad (5.1)$$

Here we have introduced a time-dependent matrix operator $\mathbf{B}(\Omega_B,t)$ which is given by

$$\mathbf{B}(\Omega_B,t)\equiv\Delta\Omega_B+\frac{\chi_0}{2}\Sigma F_0(\mathbf{r}(t)) + \frac{\chi_1}{2}[\Delta F_-(\mathbf{r}(t))+\Delta^{\mathrm{T}}F_+(\mathbf{r}(t))]. \quad (5.2)$$

As follows from the previous section, when motions are sufficiently fast, the effect of the matrix protons vanishes. On the other hand, if one is interested in calculating just an FID, which decays to zero after several hundred nanoseconds or less in a typical ESR experiment, one can neglect the bath term completely since it would yield a decay only in the microsecond time scale.[5,8] The latter circumstance can be also revealed in our theory by substituting the numerical values for the gyromagnetic ratios of the electron and proton in Eq. (3.13) for a typical proton concentration of $10^{22}\,\mathrm{cm}^{-3}$. In the case of spin echoes, one can first calculate the echo signal without the effect of the bath, and then simply multiply the final result in the time domain by Eq. (3.13) due to the above time scale separation. One can easily calculate the matrix-exponential operator in Eq. (5.1) containing $\mathbf{B}(\Omega_B,t)$ only [i.e., without the bath terms, $\mathbf{C}^{(ij)}$]. The latter has the form of a dressed direct-product sum, the exponential function of which leads to a product of N terms by virtue of Eq. (4.3). Assuming that all $A-B$ pairs are stochastically equivalent, the motionally averaged FID becomes

$$\frac{G(t)}{Z}=\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}e_O^{-i\int_0^t dt'\mathbf{B}(\Omega_B,t')}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\rangle^N. \quad (5.3)$$

To evaluate Eq. (5.3) in the thermodynamic limit ($N,V\to\infty$), one can use the Markov method[3,21] which leads to

$$\begin{aligned}G(t)&=Z\lim_{N,V\to\infty}\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}e_O^{-i\int_0^t dt'\mathbf{B}(\Omega_B,t')}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\rangle^N\\&=Z\lim_{N,V\to\infty}2^N\left[1-\frac{C}{N}\right.\\&\quad\left.\times\left\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}\frac{\mathbf{1}-e_O^{-i\int_0^t dt'\mathbf{B}(\Omega_B,t')}}{2}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\right\rangle'\right]^N\\&=\frac{q}{2}\exp-C\left\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}\frac{\mathbf{1}-e_O^{-i\int_0^t dt'\mathbf{B}(\Omega_B,t')}}{2}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\right\rangle',\end{aligned} \quad (5.4)$$

where the prime means averaging over the unnormalized equilibrium distribution, i.e., when the volume V has been factored out of the averaging, cf. Ref. 3.

In the same manner as we have calculated the FID, Eq. (5.4), the motionally averaged echo signal becomes

$$\begin{aligned}\frac{G(t)}{Z}&=\mathbf{g}^{\mathrm{T}}\langle e_O^{-i\int_\tau^t dt'\mathbf{H}^x(t')}\mathbf{X}_{(\pi)_x}e_O^{-i\int_0^\tau dt'\mathbf{H}^x(t')}\rangle\mathbf{g}(0)\\&=\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}e_O^{-i\int_\tau^t dt'\mathbf{B}(\Omega_B,t')}\\&\quad\times e_O^{i\int_0^\tau dt'\mathbf{B}(-\Omega_B,t')}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\rangle^N.\end{aligned} \quad (5.5)$$

In the thermodynamic limit, N, $V\to\infty$ but $C=N/V=\mathrm{const}$, the Markov averaging leads to

$$\begin{aligned}G(t)&=\frac{q}{2}\exp-C\left\langle(\mathbf{i}_\alpha+\mathbf{i}_\beta)^{\mathrm{T}}\right.\\&\quad\left.\times\frac{\mathbf{1}-e_O^{-i\int_\tau^t dt'\mathbf{B}(\Omega_B,t')}e_O^{i\int_0^\tau dt'\mathbf{B}(-\Omega_B,t')}}{2}(\mathbf{i}_\alpha+\mathbf{i}_\beta)\right\rangle',\end{aligned} \quad (5.6)$$

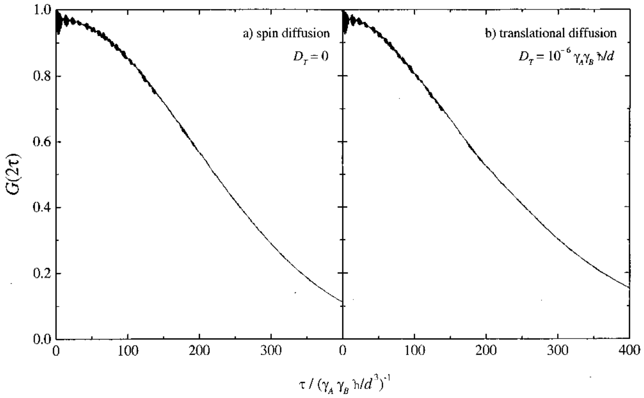

FIG. 2. A comparison between the electron spin-echo envelope decay due to (a) "spin diffusion," and (b) translational diffusion at ultraslow motions, $D_T = 10^{-6}$ (in units of $\gamma_A\gamma_B\hbar/d$). If the distance of closest approach is chosen to be $d = 3$ Å, this value corresponds to $D_T = 1.7\times10^{-14}\ \mathrm{cm^2/s}$ for electron–proton interactions. The proton concentration is set to be $C = 8.8\times10^{21}\ \mathrm{cm^{-3}}$ in all subsequent calculations; (10^6 protons in a sphere having a radius of 100d). The proton modulation frequency is chosen to be $\Omega_B = 5\gamma_A\gamma_B\hbar/d^3 = 14.6$ MHz. With the above values, the total time scale corresponds to about 20 μs. At this very low value of the translational diffusion coefficient D_T the time scales of the two relaxation processes are comparable to each other.

where the prime means taking the average over an unnormalized equilibrium distribution as before.

Evaluation of the quadratic matrix forms in Eqs. (5.4) and (5.6) can be performed by solving a system of coupled stochastic Liouville equations as described in Appendix A. The rigid-limit case is considered in Appendix B.

VI. RESULTS

All numerical calculations in this paper have been performed by using MATLAB (Math Works, Inc.) in combination with the *expv*-routine.[22] The latter is ideally suited for handling exponential functions of large sparse matrices in the time domain, especially in the rigid limit. The proton concentration has been set to $C = 8.8\times10^{21}\ \mathrm{cm^{-3}}$ in all calculations, which corresponds to $N = 10^6$ protons contained in a sphere having a radius of 100d, where d is the distance of closest approach between the spin-bearing molecules set here at 3 Å. A sphere of this size effectively corresponds to the thermodynamic limit, the convergence to which can be checked in the same manner as has been done in Ref. 3. Note that in order to have the same concentration in Eq. (3.13) as in Eqs. (5.4) and (5.6), one has to set $C = a^{-3} = N/[4\pi/3(100d)^3]$, from which $a \approx 1.6\,d$. The motionally averaged exponential quadratic forms that appear in Eqs. (5.4) and (5.6) have been evaluated by solving the system of coupled stochastic Liouville equations (SLE), Eqs. (A2a)–(A2d).

Figure 2 shows a comparison between the two relaxation mechanisms for the echo amplitude. The first is due to a magnetization loss due to the matrix protons, Fig. 2(a), and the second arises from ultraslow translational diffusion, Fig. 2(b). The effect of the matrix protons (spin diffusion) has been calculated by multiplying Eq. (3.13) and Eq. (5.6) in the rigid limit ($D_T = 0$), which was justified above due to their time-scale separation [cf. discussion after Eq. (5.2)]. The effects of motional averaging have been calculated from Eq. (5.6) by solving the system of SLE with $D_T = 10^{-6}$ (in units of $\gamma_A\gamma_B\hbar/d$). At this very low translational diffusion rate ($D_T \approx 1.7\times10^{-14}\ \mathrm{cm^2/s}$ if $d = 3$ Å), the timescales of the two relaxation processes are comparable to each other. By substituting the numerical values for the gyromagnetic ratios of the electron and proton, it can be seen that this range corresponds to times longer than 10 μs for the given proton concentration, C.

Spin-echo envelope modulation curves obtained from solving Eq. (5.6) at different values of the translational diffusion coefficient for the relative motion of spins A and B (cf. Appendix A). D_T are shown in Fig. 3. Increasing the translational diffusion coefficient decreases the modulation amplitude and results in a much faster decay than would

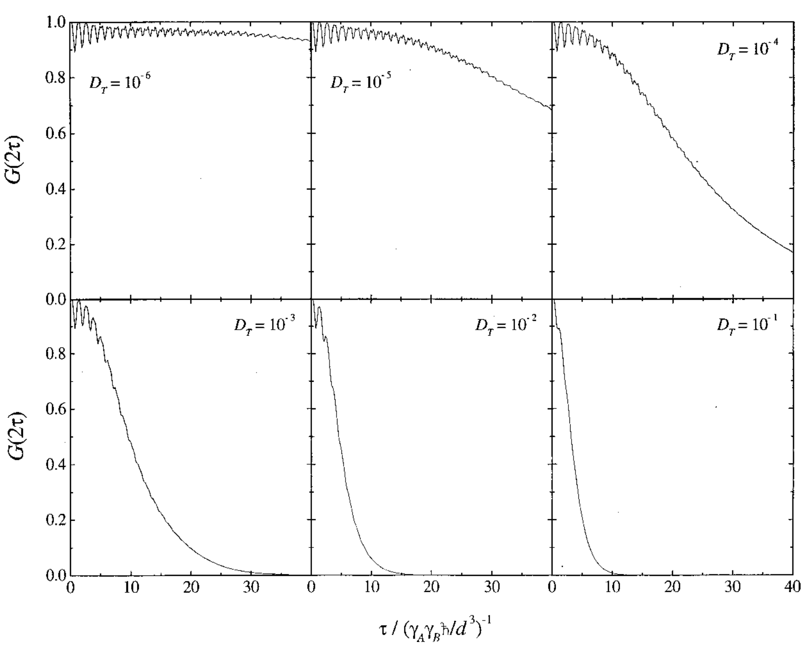

FIG. 3. Spin echo envelope modulation and decay at different values of the translational diffusion coefficient D_T in units of $\gamma_A\gamma_B\hbar/d$ as indicated on the plots. Increasing D_T decreases the modulation amplitude and results in a much faster decay than would result from the "spin diffusion" mechanism. Note that the effect of spin diffusion only decreases when motions become faster, and vanishes completely in the Redfield limit, cf. the text.

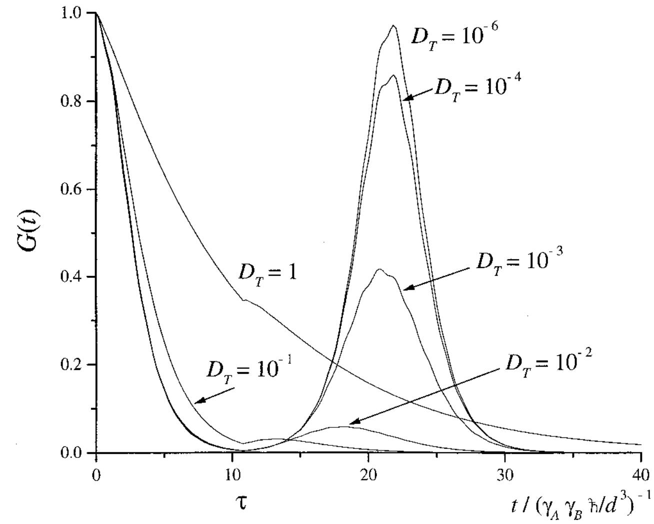

FIG. 4. Spin echoes for an AB_N system calculated at various rates of translational diffusion, D_T. Increasing the motional rate decreases the echo amplitude and shifts the echo maximum towards shorter times. Note that an appreciable refocusing is achieved in the slow to intermediate motional regime as opposed to a system of like spins, cf. Ref. 1.

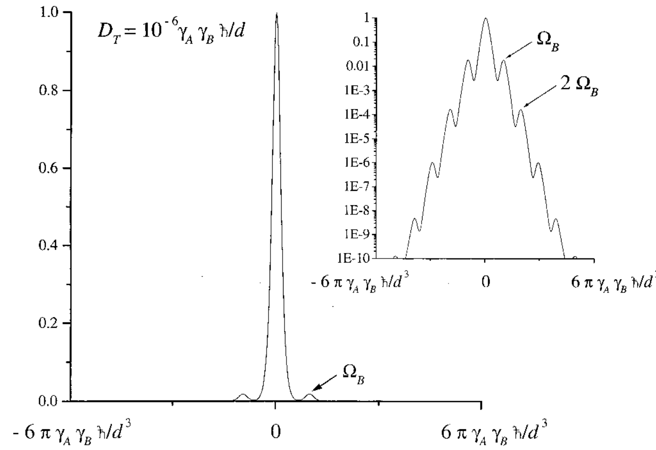

FIG. 6. Solid-state spectra of spin A interacting with a bath of N spins B calculated from solving the system of SLE's in the thermodynamic limit, $D_T = 10^{-6}$ (in units of $\gamma_A \gamma_B \hbar/d$). Here $\Omega_B = 3$ (in units of $\gamma_A \gamma_B \hbar/d^3$). Weak forbidden transitions at $\pm\Omega_B$ are seen. The magnified inset plotted on a semilogarithmic scale shows the forbidden multiquantum transitions up to the fourth order. Note that at such a relatively high concentration of spins B the spectral lines are almost Gaussian.

arise from the spin diffusion of the matrix protons. Note that the latter mechanism can only decrease in importance with motions, since the motions remove positional correlations among the protons. Furthermore, in Sec. IV we have shown that in the fast motional regime the proton coupling terms have no effect on the A-spin signal. Therefore, at faster motions the decay of the echo amplitude is due predominantly to translational diffusion.

Spin echoes for an AB_N system under the conditions of selective excitation of spin A are shown in Fig. 4 for different motional rates D_T. Modulation due to the Larmor frequency Ω_B of the B spins can be seen. Here an appreciable refocusing is achieved even in the intermediate motional regime. This has to be compared to a system of like spins, where the generation of higher-order coherences after the intermediate pulse suppresses the echo formation.[1] As can also be seen from Fig. 4, increasing the motional rate D_T further decreases the echo amplitude and shifts it towards shorter times. The onset of fast motions, i.e., where there is little or no refocusing, corresponds to $D_T = \gamma_A \gamma_B \hbar/d$. Note that this value of D_T corresponds to the range of the translational diffusion rates in lipid membranes, ($D_T \approx 10^{-8}$ cm^2/s) which implies that in this case no effect of spin diffusion on ESR spectra is expected.

The behavior of the phase memory times $T_M^{(1/2)}$, i.e., at which the echo amplitude decays by a half, versus the translational diffusion rate, D_T is illustrated in Fig. 5. The $T_M^{(1/2)}$ values have been obtained from Figs. 3 and 4. A $T_M^{(1/2)}$-minimum can be seen near $D_T = 0.1\gamma_A \gamma_B \hbar/d$. In the intermediate to slow motional regime the $T_M^{(1/2)}$-dependence

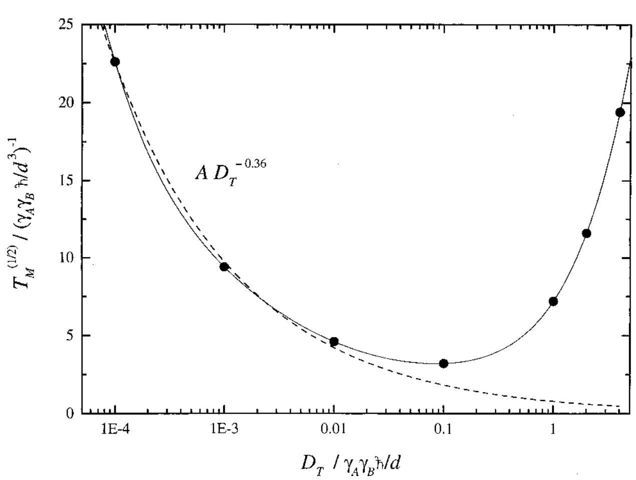

FIG. 5. Phase-memory times, $T_M^{(1/2)}$ vs the translational diffusion rate, D_T obtained from Figs. 3 and 4. A $T_M^{(1/2)}$—minimum can be seen near $D_T = 0.1\gamma_A \gamma_B \hbar/d$. Dashed line shows the limiting behavior of $T_M^{(1/2)}$ as a function of D_T for the intermediate to slow motional regime.

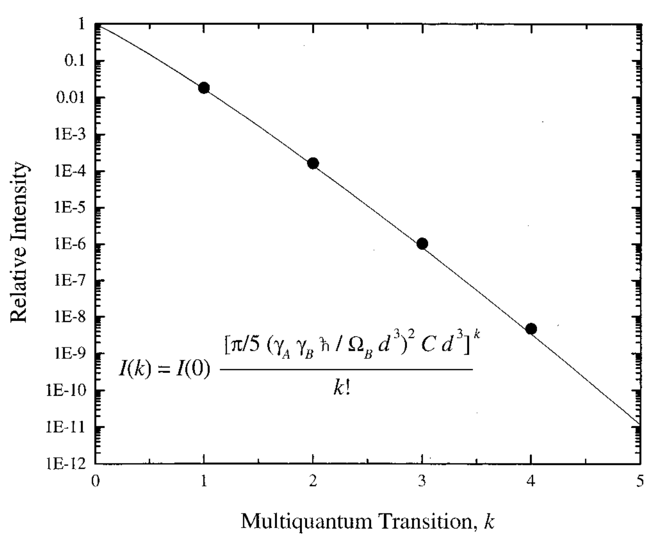

FIG. 7. Distribution of the intensities of the multiquantum transitions. The intensities are distributed according to a Poisson law and show a very good agreement with the analytical expression, Eq. (B17).

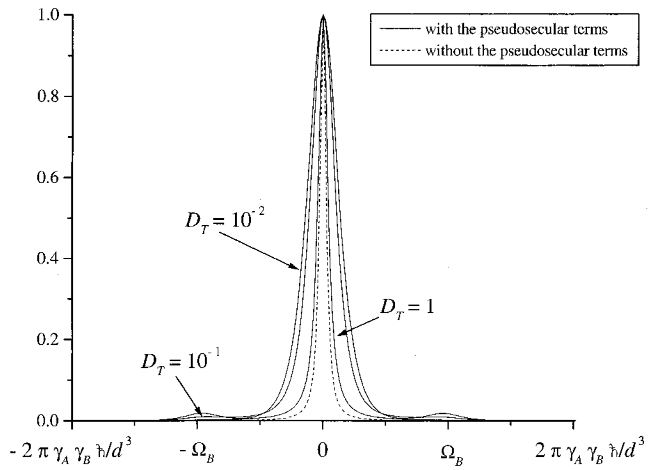

FIG. 8. Effect of translational motion on the spectra of spin A interacting with a dynamical bath of spins B. In the intermediate motional region ($D_T = 10^{-2}$) the lineshapes are between a Gaussian and a Lorentzian, but the multiquantum transitions disappear completely. The spectrum finally becomes Lorentzian at relatively large values of the diffusion coefficient (e.g., $D_T = 1$). The dashed line shows the line shape when the pseudosecular terms are dropped which is narrower than the line shape with the pseudosecular terms, since the latter has an additional contribution from terms proportional to $J_1(\Omega_B)$, in accordance with Redfield theory.

can be approximately described by the limiting behavior: $T_M^{(1/2)} = AD_T^{-0.36}$ (compare to the $D_T^{-0.32}$ behavior found previously for the homogeneous relaxation times T_2 of like spins). The fast-motional regime is described by Eq. (4.10).

A near rigid-limit absorption spectrum ($D_T = 10^{-6}\gamma_A\gamma_B\hbar/d$) calculated by using Eq. (5.4) is presented in Fig. 6. Low-intensity forbidden multiquantum transitions, corresponding to the pseudosecular terms in the Hamiltonian are observed at frequencies $\pm k\Omega_B$. A semilogarithmic plot (inset) shows the multiquantum transitions up to the fourth order, with intensities decreasing by almost 10 orders of magnitude. The weakness of these forbidden transitions is due to the very weak effects of the pseudosecular terms of Eq. (2.1a) in the thermodynamic rigid limit. This in fact is what leads to our justification of their neglect in calculating the spin-echo amplitude decay in the rigid limit [cf. discussions below Eqs. (3.6) and (B15) in Appendix B]. Note that the spectral lines are no longer Lorentzians at such a relatively high concentration of spins B. This range of concentrations corresponds to an intermediate region between the two limiting cases given by Eqs. (B15), and in this range the line shapes cannot be written in terms of simple analytical functions.

Figure 7 shows the distribution of intensities for the multiquantum transitions as measured from the spectrum and those calculated from the analytical expression, Eq. (B17). A very good agreement is obtained, which indicates that the intensities of the multiquantum transitions are distributed according to a Poisson law in the rigid limit.

The effect of the translational motion on averaging out the multiquantum transitions is illustrated in Fig. 8. When the motion becomes fast, the multiquantum transitions collapse into a single Lorentzian having a width larger than when the pseudosecular terms are dropped. This is in agreement with the fast-motional Redfield theory, which also predicts an additional contribution from the terms proportional to the first-order spectral densities, $J_1(\Omega_B)$, arising from the pseudosecular terms, cf. Eq. (4.10).

VII. SUMMARY AND CONCLUSIONS

Two channels of magnetic-resonance relaxation for spin A interacting with an infinite bath of spins B have been considered in the present paper. The first is the relaxation due to the interactions amongst the B-spins, usually called spin diffusion, and the second is the thermal motions of the spin-bearing molecules. Both mechanisms lead to modulation of the interactions of spin A with spins B, which include the electron-spin echo envelope modulation (ESEEM) and the echo-envelope decay. A careful consideration of the details of the dipolar coupling of spin A to all the B spins in the presence of $B-B$ dipolar interactions makes it possible to achieve a unified treatment of the above collective (or spin-diffusion) effects due to the B spins. The direct-product decomposition of the multispin density states proposed in Paper I,[1] allows one to consider spin A and all the spins B as a single quantum system without the need to distinguish between the nearby and distant protons. Moreover, it allows one to effectively disentangle the relevant part of the Hamiltonian from the remaining part that either cannot be observed experimentally, or does not influence the signal appreciably.

In the rigid limit, the echo envelope decay is due to the induced flip–flops of the proton spins caused by the $I_\pm^{(i)} I_\mp^{(j)}$ terms of the dipolar Hamiltonian. This mechanism is similar to spin diffusion, albeit treated here as a coherent process. The first-order commutator expansion of the superoperator time propagator has been evaluated, which results in a decay of the form $\exp(-AC^2\tau^2)$ in the limit of an infinitely large bath. Higher terms in τ (arising from double commutators and so on) have been assumed to have no appreciable effect over the time scale available to experiment. It can be anticipated that higher-order terms (such as τ^3) would become comparable with the τ^2 term only at sufficiently long times where the signal decays almost completely. This assumption is probably not valid when the gyromagnetic ratios of spins A and B are comparable to each other, e.g., in the case of unlike electrons. This case, however would also require a consideration of different terms in the Hamiltonian, i.e., the the pseudosecular terms in Eq. (2.1a) would have to be replaced by the flip–flop terms.

The results have been compared to a model[7] proposed nearly three decades ago based on a random frequency-modulation approach.[9] It is interesting to note that the present approach and the model of Ref. 7 give similar final expressions for the echo-envelope decay (apart from the constant prefactor in the exponential and a small difference from the observed τ^2 power law). However, the model of Ref. 7 considers the local field modulation at the electron as an entirely random process. By contrast, here we have considered proton spin flips as a coherent process, which is shown to become dissipative in the thermodynamic limit. It is noteworthy that in the case of like spins, the flip–flop terms of the dipolar Hamiltonian, i.e., $I_\pm^{(i)} I_\mp^{(j)}$ are found to have no appreciable effect on the T_2-processes;[1] whereas in the case of unlike spins they yield an irreversible decay of the spin-echo amplitude in the rigid limit.

In the presence of sufficiently fast motions when one can restrict oneself to the second-order generalized cumulant expansion for the motionally averaged FID, the effect of the flip–flop terms of the matrix protons has been shown to vanish completely. At very slow motions, there exists a time scale separation between the spin-echo envelope decay due to the matrix protons and the FID arising from the $A-B$ interactions. Therefore, one can first solve for the FID or echo neglecting the effect of the bath and then multiply the result by Eq. (3.13) in the time domain.

The effect of translational motion on the spin echoes has been investigated by solving a system of stochastic Liouville equations. At a very slow translational diffusion coefficient of $D_T \sim 10^{-14}\,\text{cm}^2/\text{s}$, the decay due to motional diffusion has been found comparable to that due to the spin-diffusion process. An average molecular displacement during a time of $\tau = 10\,\mu\text{s}$ would be $(6D_T\tau)^{1/2} = (6\times 1.7\times 10^{-14}\,\text{cm}^2/\text{s} \times 10^{-5}\,\text{s})^{1/2} \approx 0.1\,\text{Å}$, which may arise from positional fluctuations in glasses, for example. Thus, in the presence of ultraslow fluctuations, it may become difficult to distinguish between the two relaxation mechanisms. At faster motional rates, the decay of the echo envelope is found to be governed predominantly by the motions (e.g., translational diffusion) which readily overtake the coherent mechanism in importance. By contrast, the coherent effect of the matrix protons can only decrease when positional correlations amongst the protons are removed, vanishing completely in the Redfield limit.

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APPENDIX A: MOTIONAL AVERAGING OF THE EXPONENTIAL QUADRATIC FORM BY STOCHASTIC LIOUVILLE EQUATIONS

To evaluate the motionally averaged quadratic form in Eq. (5.4), we assume a stationary Markov process for the interspin distance $\mathbf{r}$ and introduce an auxiliary vector function $\mathbf{g}(\mathbf{r},t)$, such that

$$\frac{G(t)}{Z} = [(\mathbf{i}_\alpha + \mathbf{i}_\beta)^{\mathrm{T}} \langle e_O^{-i\int_0^t dt' \mathbf{B}(\Omega_B,t')} (\mathbf{i}_\alpha + \mathbf{i}_\beta)\rangle]^N$$
$$= \left[(\mathbf{i}_\alpha + \mathbf{i}_\beta)^{\mathrm{T}} \int \mathbf{d}^3\mathbf{r}\, e_O^{(-i\mathbf{B}(\Omega_B,r)+\Gamma_r)t} \mathbf{g}(\mathbf{r},0)\right]^N$$
$$= \left[\int \mathbf{d}^3\mathbf{r} (\mathbf{i}_\alpha + \mathbf{i}_\beta)^{\mathrm{T}} \mathbf{g}(\mathbf{r},t)\right]^N. \tag{A1}$$

The four components of the vector $\mathbf{g}(\mathbf{r},t)$ can then be evaluated by solving the system of coupled stochastic Liouville equations, by analogy with the simpler secular-Hamiltonian case, cf. Ref. 2,

$$\frac{\partial g_+(\mathbf{r},t)}{\partial t} - (\Gamma_\mathbf{r} - i\Omega_B) g_+(\mathbf{r},t) = -i\frac{\chi_1}{2} F_-(\mathbf{r})[g_\alpha(\mathbf{r},t) + g_\beta(\mathbf{r},t)], \tag{A2a}$$

$$\frac{\partial g_\alpha(\mathbf{r},t)}{\partial t} - \Gamma_\mathbf{r} g_\alpha(\mathbf{r},t) = -i\frac{\chi_0}{2} F_0(\mathbf{r}) g_\alpha(\mathbf{r},t) - i\frac{\chi_1}{2}[F_+(\mathbf{r}) g_+(\mathbf{r},t) + F_-(\mathbf{r}) g_-(\mathbf{r},t)], \tag{A2b}$$

$$\frac{\partial g_\beta(\mathbf{r},t)}{\partial t} - \Gamma_\mathbf{r} g_\beta(\mathbf{r},t) = +i\frac{\chi_0}{2} F_0(\mathbf{r}) g_\beta(\mathbf{r},t) - i\frac{\chi_1}{2}[F_+(\mathbf{r}) g_+(\mathbf{r},t) + F_-(\mathbf{r}) g_-(\mathbf{r},t)], \tag{A2c}$$

$$\frac{\partial g_-(\mathbf{r},t)}{\partial t} - (\Gamma_\mathbf{r} + i\Omega_B) g_-(\mathbf{r},t) = -\frac{i\chi_1}{2} F_+(\mathbf{r})[(g_a \mathbf{r},t) + g_\beta(\mathbf{r},t)], \tag{A2d}$$

with initial conditions $g_\alpha(\mathbf{r},0) = g_\beta(\mathbf{r},0) = 1$ and $g_+(\mathbf{r},0) = g_-(\mathbf{r},0) = 0$. Inspection of the system of Eqs. (A2a)–(A2d) leads to $g_\alpha(\mathbf{r},t) = g_\beta^*(\mathbf{r},t)$ and $g_+(\mathbf{r},t) = -g_-^*(\mathbf{r},t)$. Therefore, the observed signal, $g_\alpha(\mathbf{r},t) + g_\beta(\mathbf{r},t)$, is real.

For the functions $g_\epsilon(\mathbf{r},t)$ or, alternatively their Fourier or Fourier–Laplace transforms $\tilde{g}_\epsilon(\mathbf{r},\omega)$, we construct spherical-harmonic expansions in the form

$$g_\epsilon(\mathbf{r},t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{g_{\epsilon,m}^{(l)}(r,t)}{r} Y_m^{(l)}(\theta,\phi). \tag{A3}$$

Expansion (A3) is then substituted into the system of Eqs. (A2a)–(A2d) to establish the coupling among various coefficients of the expansion using the orthonormality property of the spherical harmonics. From the properties of the Clebsch–Gordan coefficients it becomes clear that $g_{\alpha,0}^{(l)}(\mathbf{r},\omega)$ and $g_{\beta,0}^{(l)}(\mathbf{r},\omega)$ will be coupled to $g_{\pm,\mp1}^{(l)}(\mathbf{r},\omega)$, and that all l's will be even. Thus, the stochastic Liouville operator $\mathbf{L}$ is given in terms of the following block-matrix equation

$$\frac{\partial \mathbf{g}(\mathbf{r},t)}{\partial t} = -\begin{pmatrix} -\hat{\Gamma}_\mathbf{r} + i\Omega_B & iD & iD & O \\ iD^{\mathrm{T}} & -\hat{\Gamma}_\mathbf{r} + iC & O & -id^{\mathrm{T}} \\ iD^{\mathrm{T}} & O & -\hat{\Gamma}_\mathbf{r} - iC & -iD^{\mathrm{T}} \\ O & -iD & -iD & -\hat{\Gamma}_\mathbf{r} - i\Omega_B \end{pmatrix} \times \mathbf{g}(\mathbf{r},t) \equiv -\mathbf{L}\mathbf{g}(\mathbf{r},t), \tag{A4}$$

where $\hat{\Gamma}_\mathbf{r}$ is the reduced diffusion operator for the relative motion,[23]

$$\hat{\Gamma}_{\mathbf{r}}=D_T\left[\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}\right], \tag{A5}$$

and the elements of the tridiagonal matrices C and D are given in terms of the Clebsch–Gordan coefficients,

$$\begin{aligned} c_{ll'}&=\frac{\chi_0}{r^3}\int \sin\theta d\theta d\phi Y_0^{(l)}(\theta,\phi)^* Y_0^{(2)}(\theta,\phi)Y_0^{(l')}(\theta,\phi)\\ &=\frac{\chi_0}{r^3}\sqrt{\frac{5}{4\pi}\frac{(2l'+1)}{(2l+1)}}\langle l'200|l'2l0\rangle^2 \end{aligned} \tag{A6}$$

$$\begin{aligned} d_{ll'}&=\frac{\chi_1}{r^3}\int \sin\theta d\theta d\phi Y_{-1}^{(l)}(\theta,\phi)^* Y_1^{(2)}(\theta,\phi)^* Y_0^{(l')}(\theta,\phi)\\ &=\frac{\chi_1}{r^3}\sqrt{\frac{5}{4\pi}\frac{(2l+1)}{(2l'+1)}}\langle l200|l2l'0\rangle\langle l2-11|l2l'0\rangle. \end{aligned}$$

To treat translational effects in r, we use the finite-difference method to approximate the differential operator $\Gamma_{\mathbf{r}}$ in Eq. (A5) as described in Refs. 2 and 23.

APPENDIX B: INTENSITY DISTRIBUTION OF THE FORBIDDEN MULTIQUANTUM TRANSITIONS FOR SOLID-STATE MANY-BODY SPECTRA

In the absence of motions, $\Gamma_{\mathbf{r}}=0$, the system of equations (A2a)–(A2d) can be solved analytically. To do this, we rewrite it as a single equation for the real part of $g_\alpha(\mathbf{r},\omega)$, $\mathrm{Re}\, g_\alpha(\mathbf{r},\omega)\equiv u(\mathbf{r},t)$

$$\frac{\partial^2 u(\mathbf{r},t)}{dt^2}+\left[\frac{\chi_0^2}{4}F_0(\mathbf{r})^2+\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})\right]u(\mathbf{r},t) =\chi_1^2\Omega_BF_+(\mathbf{r})F_-(\mathbf{r})\int_0^t dt'\,u(\mathbf{r},t')\sin\Omega_B(t-t'), \tag{B1}$$

subject to the initial conditions: $u(\mathbf{r},0)=1$ and $\partial u(\mathbf{r},0)/\partial t=0$. This equation can be most readily solved by the method of Laplace transforms, which yields

$$u(\mathbf{r},t)=\frac{(a^2-\Omega_B^2)\cos at-(b^2-\Omega_B^2)\cos bt}{a^2-b^2}, \tag{B2}$$

where

$$a^2,b^2=\frac{1}{2}\left[\frac{\chi_0^2}{4}F_0(\mathbf{r})^2+\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})+\Omega_B^2\right]\pm\frac{1}{2}\sqrt{\left[\frac{\chi_0^2}{4}F_0(\mathbf{r})^2+\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})-\Omega_B^2\right]^2+4\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})\Omega_B^2}. \tag{B3}$$

If $\Omega_B\gg\chi_{0,1}F_{0,\pm}(\mathbf{r})$, then

$$u(\mathbf{r},t)\approx\cos\frac{\chi_0}{2}F_0(\mathbf{r})t+\frac{\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})}{\Omega_B^2}\times\cos\left[\Omega_B+\frac{\chi_1^2F_+(\mathbf{r})F_-(\mathbf{r})}{2\Omega_B}\right]t. \tag{B4}$$

Where the first term corresponds to the allowed transitions, and the second gives the forbidden transitions.

At constant r, the Fourier transformation of the allowed transitions is given by the well-known Pake formula

$$\begin{aligned}\tilde{u}_0(r,\omega)&=2\pi\int_{-1}^1 dx\,\pi\delta\left[\frac{5}{16\pi}\frac{\chi_0^2}{r^3}\frac{3x^2-1}{2}-\omega\right]\\ &=\frac{4\pi^2r^3}{\sqrt{3}\chi_0'\sqrt{\frac{2\omega r^3}{\chi_0'}+1}},\quad -\frac{\chi_0'}{2r^3}<\omega\leqslant\frac{\chi_0'}{r^3},\end{aligned} \tag{B5}$$

where we introduced a reduced coupling constant, $\chi_0'\equiv\gamma_A\gamma_B\hbar$. When integrated over r^2dr from d to $(\chi_0'/\omega)^{-1/3}$ for $\omega>0$, and from d to $(\chi_0'/2|\omega|)^{-1/3}$ for $\omega<0$, the total solid line shape for the allowed transitions becomes

$$\begin{aligned}\tilde{u}_0(\omega)&=\int r^2dr[\tilde{u}_0(r,\omega)+\tilde{u}_0(r,-\omega)],\\ \int r^2dr\tilde{u}_0(r,\omega)&=\frac{4\pi^2\chi_0'}{9\sqrt{3}\omega^2}\sqrt{1+\frac{2\omega d^3}{\chi_0'}}\left(1-\frac{\omega d^3}{\chi_0'}\right),\\ &-\frac{\chi_0'}{2d^3}<\omega\leqslant\frac{\chi_0'}{d^3},\end{aligned} \tag{B6}$$

i.e., it behaves asymptotically as ω^{-2} near $\omega=0$.

The line shape for the forbidden transition in the solid-state limit can be calculated in a manner analogous to the calculation of the Pake pattern (i.e., the allowed transitions), which yields for one of the two symmetric branches near $\omega=\pm\Omega_B$

$$\begin{aligned}\tilde{u}_1(r,\omega)&=2\pi\frac{15}{8\pi}\frac{\chi_1^2}{\Omega_B^2}\int_{-1}^1 dx\frac{x^2(1-x^2)}{r^3}\times\pi\delta\left[\Omega_B+\frac{15}{8\pi}\frac{\chi_1^2}{\Omega_B}\frac{x^2(1-x^2)}{r^3}-\omega\right]\\ &=\frac{2\pi^2}{\Omega_B}\sqrt{\frac{(8\Omega_Br^6/\chi_1'^2)(\omega-\Omega_B)}{1-\sqrt{(8\Omega_Br^6/\chi_1'^2)(\omega-\Omega_B)}}},\\ &\Omega_B\leqslant\omega<\Omega_B+\frac{\chi_1'^2}{8\Omega_Br^6},\end{aligned} \tag{B7}$$

and zero otherwise. In the above expression we made the substitution, $x=\cos\theta$, and introduced a reduced coupling constant, $\chi_1'\equiv 3\gamma_A\gamma_B\hbar/2$. As one can see, the forbidden transition will result in a very narrow line having a breadth of $\chi_1'^2/8\Omega_B^2 r^6$ in units of Ω_B, and a singularity at $\omega=\Omega_B+\chi_1'^2/8\Omega_B r^6$.

When integrated over r^2dr from d to $r_{\max}=[8\Omega_B(\omega-\Omega_B)/\chi_1'^2]^{-1/6}$, Eq. (B7) becomes

$$\tilde{u}_1(\omega)=\frac{8\pi^2 d^3}{9\Omega_B\xi(\omega)}\sqrt{1-\xi(\omega)}[1+\xi(\omega)/2], \tag{B8}$$

$$\xi(\omega)\equiv\sqrt{\frac{8\Omega_B d^6}{\chi_1'^2}(\omega-\Omega_B)},\quad \Omega_B<\omega\leqslant\Omega_B+\frac{\chi_1'^2}{8\Omega_B d^6}.$$

The singularity is now at exactly Ω_B, and the lineshape has an asymptotic behavior of $(\omega-\Omega_B)^{-1/2}$ near $\omega=\Omega_B$.

By substituting the two-body solution, $u(\mathbf{r},t)$ in Eq. (5.4), and using the Markov method, one can write the for the many-body FID at N, $V\rightarrow\infty$

$$\begin{aligned}G(t)&=\lim_{N\rightarrow\infty}\frac{q}{2^{N+1}}\left[\int dVg_\alpha(\mathbf{r},t)+g_\beta(\mathbf{r},t)\right]^N\\&=\lim_{N\rightarrow\infty}\frac{q}{2^{N+1}}\left[2\int dVu(\mathbf{r},t)\right]^N\\&=\lim_{N\rightarrow\infty}\frac{q}{2}\left\{1-\frac{C}{N}\int dV[1-u(\mathbf{r},t)]\right\}^N\\&=\frac{q}{2}\exp\left\{-C\int dV[1-u(\mathbf{r},t)]\right\}=\frac{q}{2}\exp\left[C\int_0^t\frac{\partial u(t)}{\partial t}\right],\end{aligned} \tag{B9}$$

where $q=\hbar\Omega_A/kT$.

The corresponding many-body line shape is obtained from the integral equation containing the two-body line shape, cf. Ref. 3,

$$-i\omega\tilde{G}(\omega)+\frac{iC}{2\pi}\int_{-\infty}^{+\infty}(\omega-\omega')\tilde{u}(\omega-\omega')\tilde{G}(\omega')d\omega'=G(0), \tag{B10}$$

where the two-body line shape $\tilde{u}(\omega)$ contains both the allowed and forbidden spectra. Here the many-body spectral function $\tilde{G}(\omega)$ is understood as the *Fourier–Laplace* transformation of $G(t)$, since the latter is a decaying function even in the solid-state limit. By contrast, the two-body FID's, $u(t)$, are expressed in the rigid limit in terms of cosine functions, cf. Eq. (B2), and thus have to be treated by conventional Fourier transforms. One can estimate the contribution of the forbidden transition relative to the allowed transitions by calculating the convolution integral in Eq. (B10). For the allowed transitions, Eq. (B6), one has

$$\begin{aligned}&\int(\omega-\omega')\tilde{u}_0(\omega-\omega')\tilde{G}(\omega')d\omega'\\&=\int_{-\chi_0'/d^3}^{\chi_0'/d^3}\omega'\tilde{u}_0(\omega')\tilde{G}(\omega-\omega')d\omega'\\&=\frac{4\pi^2\chi_0'}{9\sqrt{3}}\left[\int_{-\chi_0'/2d^3}^{\chi_0'/d^3}\frac{\tilde{G}(\omega-\omega')}{\omega'}\sqrt{1+\frac{2\omega'd^3}{\chi_0'}}\right.\\&\quad\times\left(1-\frac{\omega'd^3}{\chi_0'}\right)d\omega'+\int_{-\chi_0'/d^3}^{\chi_0'/2d^3}\frac{\tilde{G}(\omega-\omega')}{\omega'}\\&\quad\left.\times\sqrt{1-\frac{2\omega'd^3}{\chi_0'}}\left(1+\frac{\omega'd^3}{\chi_0'}\right)d\omega'\right].\end{aligned} \tag{B11}$$

The convolution integral corresponding to the forbidden transitions, Eq. (B8), can be estimated by assuming that $\tilde{G}(\omega)$ varies slowly within the narrow interval from Ω_B to $\chi_1'^2/8\Omega_B d^3$, viz.,

$$\begin{aligned}&\int_{\Omega_B}^{\Omega_B+\chi_1'^2/8\Omega_B d^6}\omega'\tilde{u}_1(\omega')\tilde{G}(\omega-\omega')d\omega'\\&\approx\Omega_B\tilde{G}(\omega-\Omega_B)\int_{\Omega_B}^{\Omega_B+\chi_1'^2/8\Omega_B d^6}\tilde{u}_1(\omega')d\omega'\\&=\frac{8\pi^2\chi_1'^2}{45\Omega_B d^3}\tilde{G}(\omega-\Omega_B),\end{aligned} \tag{B12}$$

plus the corresponding counterpart at $\omega=-\Omega_B$. The use of the inverse Fourier transformation followed by the application of the shift theorem for Fourier transforms yields

$$\begin{aligned}&\frac{\partial G(t)}{\partial t}+G(t)\frac{4\pi^2\chi_0'}{9\sqrt{3}}\frac{iC}{2\pi}\\&\times\int_{-\chi_0'/2d^3}^{\chi_0'/d^3}-2i\frac{\sin\omega't}{\omega'}\sqrt{1+\frac{2\omega'd^3}{\chi_0'}}\left(1-\frac{\omega d^3}{\chi_0'}\right)d\omega'\\&+i\frac{4\pi\chi_1'^2C}{45\Omega_B d^3}(e^{-i\Omega_B t}-e^{i\Omega_B t})G(t)=0.\end{aligned} \tag{B13}$$

This equation can be integrated which leads to a rather interesting behavior for the many-body FID which can be written in a compact form

$$\begin{aligned}G(t)=G(0)\exp&\left[-\frac{4\pi}{9\sqrt{3}}\chi_0'C\int_0^t dt'\int_0^{t'}dt''\right.\\&\left.\times\int_{-1/2}^{1}\cos\left(\frac{\chi_0't''}{d^3}x\right)\sqrt{1+2x}(1-x)dx\right]\\&\times\exp\left[\frac{2\pi}{5}\left(\frac{\chi_0'}{\Omega_B d^3}\right)^2Cd^3(\cos\Omega_B t-1)\right].\end{aligned} \tag{B14}$$

The first exponential part of Eq. (B14) has two limiting line shape behaviors, depending on the density of perturbers B

$$\exp\left[-\frac{4\pi}{9\sqrt{3}}\chi_0' C\int_0^t dt'\int_0^{t'}dt'' \times\int_{-1/2}^{1}\cos\left(\frac{\chi_0' t''}{d^3}x\right)\sqrt{1+2x}(1-x)dx\right] = \begin{cases}\exp\left(-\frac{4\pi^2}{9\sqrt{3}}\chi_0' Ct\right), & \text{Lorentzian},\quad Cd^3\ll 1\\ \exp\left(-\frac{2\pi}{15}\left(\frac{\chi_0'}{d^3}\right)^2 Cd^3t^2\right), & \text{Gaussian},\quad Cd^3\gg 1.\end{cases} \tag{B15}$$

The first case corresponds to low concentrations of spins B, which result in a simple exponential decay with the rate given by the classical Anderson formula,[24] $1/T_2^* = 4\pi^2\gamma_A\gamma_B\hbar C/9\sqrt{3}$. At large enough concentrations of the B-spins, there may be a non-negligible effect of the oscillating (Ω_B-containing) part of Eq. (B14) corresponding to the forbidden transitions. The conditions for this should be: $Cd^3\gg 1$, $T_2^*\gtrsim\Omega_B^{-1}$ having at the same time $\Omega_B \gg \gamma_A\gamma_B\hbar/d^3$, for which Eq. (B4) has been derived. But even for pure water (protons, $C\sim 6\times 10^{22}\,\mathrm{cm}^{-3}$, $T_2^*\sim 10^7\,\mathrm{s}^{-1}$, $\Omega_B = 14.5\,\mathrm{MHz}$) the relative intensities of the multiquantum transitions in the *rigid limit* spectra will be rather low if the distance of closest approach is $d = 3\,\text{Å}$, for which $\gamma_A\gamma_B\hbar/d^3 = 2.9\,\mathrm{MHz}$. By contrast, in the *motional-narrowing* regime the pseudo-secular terms yield considerable extra line broadening as given by the Redfield theory, cf. Eq. (4.10).

From Eq. (B14) one can obtain the distribution of intensities for the multiquantum forbidden transitions. The corresponding exponential part can be expanded into a Taylor-binomial series as

$$\exp\left[\frac{2\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3(\cos\Omega_B t-1)\right] = \sum_{n=0}^{\infty}\sum_{m=-n}^{n}\binom{2n}{n-m}\frac{(-1)^{n-m}}{n!}\left[\frac{\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3\right]^n \times\exp(-im\Omega_B t). \tag{B16}$$

Assuming for simplicity the Lorentzian (low-density) case and that $\Omega_B T_2^*\gg 1$, the intensity distribution can be calculated by applying the Fourier transform convolution theorem, which yields

$$\tilde{G}(k\Omega_B) = \frac{G(0)}{2\pi}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\int d\omega'\frac{T_2^*}{1+(k\Omega_B-\omega')^2T_2^{*2}}\binom{2n}{n-m}\frac{(-1)^{n-m}}{n!}\left[\frac{\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3\right]^n 2\pi\delta(\omega'-m\Omega_B)$$
$$\approx G(0)T_2^*\sum_{n=k}^{\infty}\binom{2n}{n-k}\frac{(-1)^{n-k}}{n!}\left[\frac{\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3\right]^n \approx G(0)T_2^*\frac{\left[\frac{\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3\right]^k}{k!}\exp\left[-\frac{2\pi}{5}\left(\frac{\gamma_A\gamma_B\hbar}{\Omega_B d^3}\right)^2 Cd^3\right], \tag{B17}$$

where we used the Stirling approximation to calculate the binomial coefficients. Thus, the fall of the intensities of the forbidden transitions is given approximately by a Poisson-type distribution.

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