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Fast-computational approach to the evaluation of slow-motion EPR spectra in terms of a generalized Langevin equation

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A Mori-type generalized Langevin equation is shown to be the only theoretical tool necessary for setting up a fast-computational method of evaluating EPR spectra. The advantages of this algorithm, concerning memory storage and time consumption, are clearly illustrated by explicitly evaluating the line shape of a nitroxide spin probe both in an isotropic liquid solution and in a liquid-crystal mesophase. This method makes theoretical EPR spectra of an orientated system in the slow-motion regime readily available. It is shown that the presence of an orientating potential renders the EPR spectrum much more sensitive to the details of molecular dynamics, thereby making this a potentially powerful tool for monitoring rotational dynamics in liquid mesophases.

I. INTRODUCTION

Electronic paramagnetic resonance spectroscopy as dealt with by the stochastic Liouville equation (SLE) theory[1] has a well established theoretical background leaving open only one major problem. As pointed out by Kubo,[2] the detailed balance requirement is not satisfied by the standard form of the SLE theory resulting in an incorrect equilibrium distribution. Although, in principle, it would be possible to amend the theory from this flaw,[3] it is widely believed[4] that in the standard experimental conditions this does not lead to any significant discrepancy between theory and experiment.

Within the environment of researchers currently involved in experimental investigation of both base[5] and application nature[6] there is a strong demand for a fast-computational algorithm to be built up. It has been shown, for example, that the evaluation of Ref. 5(b) involves several hours of computer time. These computational difficulties are usually met when dealing with the slow-motion regime.[4–9] This regime is characterized by the breakdown of the complete separability between the "macroscopic" time (the spin relaxation time) and the "microscopic" time (in our case the rotational diffusion time of the molecule containing the resonanting magnetic spin). A clear-cut separation between the two time scales is the basic theoretical requirement for simplified master equations of the Markovian type to be built up.

Attempts to solve this intriguing problem have recently been made by a few research groups.[7–9] A major purpose of the present paper is to make readily usable by the researchers of this area the findings of Giordano *et al.*, which are so far available only in a short and very preliminary version.[7] This is a more detailed report which also includes significant theoretical improvements such as those recently arrived at in Ref. 10 and, especially, those of Ref. 11. Our computational method will be shown to completely rely on a generalized Langevin equation theory. Similar theoretical developments have recently been made by Lee[12] with applications to the spin van der Waals model and two-dimensional electronic systems. To enlighten the nature of our approach we shall apply our computational algorithm to evaluating EPR line shapes in the slow-motion region.

The plan of the present paper is as follows. In Sec. II we shall make a detailed picture of the general theory on which our algorithm is based. Rather than involving the heavy algebra of the Hankel determinants[7,13] we shall only use simple physical arguments. Our theoretical approach consists in a suitable generalization of the celebrated Mori theory[14] valid also when neither Hermitian nor anti-Hermitian properties can be invoked. This is especially useful within the context of the standard SLE theory, where the lack of a detailed balance mechanism prevents us from making Hermitian the dynamical operators driving the variable of interest.[3]

In Sec. III A we shall adapt our approach so as to make it suitable for EPR spectroscopy. Then in Sec. III B this algorithm will be applied to determining the slow-motion line shape of a spin nitroxide radical solved in an isotropic solution in a liquid-crystal mesophase.

II. GENERAL THEORY

It seems to us that the ultimate theoretical justification for all the attempts so far made[7–9] is virtually the same—mathematical in nature. Dammers *et al.*,[9] for example, based their approach on the application of Padé

approximants, whose close relationship with the continued-fraction algebra is well known.[15] Still clearer is the connection between the Lanczos algorithm[16] and the approach of Ref. 7: Both ultimately result in tridiagonal matrices. Here we show a completely physical way to our fast-computational algorithm.

According to the linear response theory,[17] the problem of determining line shapes can be traced back to determining the Laplace transform of equilibrium correlation functions such as

$$\Phi(t)=\langle A^{\dagger}(0)A(t)\rangle/\langle A^{\dagger}A\rangle \ . \tag{2.1}$$

The time evolution of the variable A is described by the following equation of motion

$$\frac{d}{dt}A=\mathscr{L}A \ , \tag{2.2}$$

where $\mathscr{L}$ is a generic dynamical operator. The simplest way of facing this problem would be to expand $\mathscr{L}$ over a suitable basis set of "vectors" and diagonalize the resulting matrix via standard procedures. This approach, however, would imply the large computer time consumption of Ref. 5 as well as memory storage problems. We shall completely bypass these difficulties.

First of all, we shall define a suitable scalar product between the two generic variables A and B, denoted by the symbol $\langle A \mid B\rangle$. In Sec. III we shall define the explicit form of this scalar product for the present theory to be effectively applied to evaluating the EPR spectra. Note also that $\Phi(t)$, Eq. (2.1), can be written in terms of this scalar product as follows:

$$\Phi(t)=\langle A \mid \exp(\mathscr{L}t) \mid A\rangle/\langle A \mid A\rangle \ . \tag{2.3}$$

This scalar product allows us to build up the following biorthogonal set of vectors:

$$\begin{aligned}
&|f_0\rangle=|A\rangle \ , \\
&P_0\equiv|f_0\rangle\langle f_0|f_0\rangle^{-1}\langle f_0| \ , \\
&|f_1\rangle\equiv(1-P_0)\mathscr{L}|f_0\rangle \ , \\
&|\tilde{f}_1\rangle\equiv(1-P_0)\mathscr{L}^{\dagger}|f_0\rangle \ ; \\
&P_1\equiv|f_1\rangle\langle\tilde{f}_1|f_1\rangle^{-1}\langle\tilde{f}_1| \ , \\
&|f_2\rangle\equiv(1-P_1)\mathscr{L}|f_1\rangle \ , \\
&|\tilde{f}_2\rangle\equiv(1-P_1^{\dagger})\mathscr{L}^{\dagger}|\tilde{f}_1\rangle ; \\
&\cdots \ .
\end{aligned} \tag{2.4}$$

We are now in a position to follow the Mori method[14] without having recourse to the requirement that $i\mathscr{L}$ of Eq. (2.2) is Hermitian. This leads us[3] to show that the kth-order correlation function

$$\Phi_k(t)\equiv\langle\tilde{f}_k \mid f_k(t)\rangle/\langle\tilde{f}_k \mid f_k\rangle \tag{2.5}$$

is related to the $(k+1)$th one via hierarchy relationship

$$\frac{d}{dt}\Phi_k(t)=\lambda_k\Phi_k(t)-\int_0^t\Delta_{k+1}^2\Phi_{k+1}(t-\tau)\Phi_k(\tau)d\tau \ , \tag{2.6}$$

where

$$\lambda_k\equiv\langle\tilde{f}_k \mid \mathscr{L} \mid f_k\rangle/\langle\tilde{f}_k \mid f_k\rangle \ , \tag{2.7}$$

$$\Delta_k^2\equiv-\langle\tilde{f}_{k+1} \mid f_{k+1}\rangle/\langle\tilde{f}_k \mid f_k\rangle \ . \tag{2.8}$$

By Laplace transforming Eq. (2.6) we obtain, in continued-fraction form,

$$\hat{\Phi}_0(z)\equiv\hat{\Phi}(z)=\cfrac{1}{z-\lambda_0+\cfrac{\Delta_1^2}{z-\lambda_1+\cfrac{\Delta_2^2}{z-\lambda_2+\cdots}}} \ . \tag{2.9}$$

Equation (2.9) is of basic importance within the context of our computer algorithm. This equation will be used to express the EPR spectra without having recourse to diagonalization procedures.

For this property to be proven useful the parameters λ_i and Δ_i^2, Eqs. (2.7) and (2.8), have to be determined in terms of the moments

$$s_n\equiv\langle A \mid \mathscr{L}^n \mid A\rangle/\langle A \mid A\rangle \tag{2.10}$$

via a procedure more efficient than that suggested by the above outlined projection algebra. Giordano *et al.*[7] used Dupuis' algorithm.[13] This method, however, is redundant in that a large amount of tedious algebra is used to rederive the generalized Langevin equation, which can be used[11] as the only starting point of our computer algorithm. This can be done as follows. Note that $\Phi(t)$ of Eq. (2.1) has to be identified with the zeroth order one of our hierarchy of correlation functions. Let us develop $\Phi_0(t)$ into a Taylor power series:

$$\Phi_0(t)=\sum_{i=0}^{N}s_i^{(0)}\frac{t^i}{i!} \quad (s_i^{(0)}\equiv s_i) \ . \tag{2.11}$$

The number N is assumed to be even. It should be made as large as possible. Then we shall develop $\Phi_1(t-\tau)$ around $t-\tau=0$ as follows:

$$\begin{aligned}
\Phi_1(t-\tau)&=\sum_{n=0}^{N-2}\frac{1}{n!}s^{(1)}(t-\tau)^n \\
&=\sum_{n=0}^{N-2}\frac{1}{n!}s_n^{(1)}\sum_{k=0}^{n}\begin{bmatrix}n\\k\end{bmatrix}t^{n-k}(-\tau)^k \ .
\end{aligned} \tag{2.12}$$

Equation (2.6) with $k=0$ allows us to express the parameters $s_n^{(1)}$ as a function of the $s_n^{(0)}$'s. After a straightforward, though tedious algebra, we obtain

$$s_m^{(1)}=\frac{s_1^{(0)}s_{m+1}^{(0)}-s_{m+2}^{(0)}}{(s_1^{(0)})^2-s_2^{(0)}}-\sum_{k=0}^{m-1}s_k^{(1)}s_{m-k}^{(0)} \ , \quad 0\le m\le N-2 \ . \tag{2.13}$$

This expression allows us to express the first $N-2$ $s_m^{(1)}$'s in terms of the first N $s_n^{(0)}$'s. In general,

$$s_m^{(i)}=\frac{s_1^{(i-1)}s_{m+1}^{(i-1)}-s_{m+2}^{(i-1)}}{(s_1^{(i-1)})^2-s_2^{(i-1)}}-\sum_{k=0}^{m-1}s_k^{(i)}s_{m-k}^{(i-1)} \ , \quad 0\le m\le N-2i \ . \tag{2.14}$$

The first N moments of $\Phi_0(t)$ allow us to get information up to

$\Phi_{N/2-1}(s_2^{(N/2-1)})$.

Transfering this information from $\Phi_0(t)$ to $\Phi_{N/2-1}$ is proven to be an easy matter when having a computer available, provided that Eq. (2.14) is used. From the definitions of Eqs. (2.4), (2.7), and (2.8) it is straightforward to get

$$\lambda_i = s_1^{(i)} , \tag{2.15}$$

$$\Delta_{i+1}^2 = (s_1^{(i)})^2 - s_2^{(i)} . \tag{2.16}$$

We have thus shown that $\hat{\Phi}_0(z)$ can be expressed in a continued-fraction form, whose expansion parameter can be given in terms of the moments s_n. The only theoretical tool we used to arrive at this important result is the generalized version of the celebrated Mori theory.[3] To completely solve the actual problem of evaluating spectra we should have available the values of the parameters s_n. For these to be evaluated in an efficient way, the peculiar structure of the dynamical operator $\mathscr{L}$ of Eq. (2.2) has to be carefully considered. In Sec. III we show in detail how this problem can be solved by focusing our attention on problems of interest for EPR spectroscopy.

III. APPLICATIONS TO THE EVALUATION OF THE EPR SPECTRA

The EPR phenomenon that we shall discuss for illustrative purposes concerns a nitroxide spin probe both in an isotropic liquid solution and a liquid-crystal mesophase. In Sec. III A we shall make the general theory of Sec. II suitable for EPR spectroscopy. In Sec. III B we shall illustrate the corresponding results.

A. Fast-computational algorithm for EPR spectroscopy

By using linear response theory[17] we can express the EPR spectrum as follows:

$$I(\omega) = \mathrm{L}\,\Phi(t) \equiv \mathrm{L}\,\langle S_-(0) S_+(t)\rangle / \langle S_- S_+\rangle \equiv \mathrm{L}\,\mathrm{Tr}[S_- \exp(iLt) S_+ / \langle S_- S_+\rangle] . \tag{3.1}$$

The symbol $\mathrm{L}\,[\Phi(t)]$ denotes the Laplace transform of the correlation function $\Phi(t)$. The variable A of Sec. II has to be identified now with the spherical component $S_+ = S_x + iS_y$ of the spin angular momentum S. The rigorous quantum-mechanical Liouvillian L is defined by

$$L(\cdots) = \mathscr{H}^{\times}(\cdots) \equiv [\mathscr{H}, \cdots] . \tag{3.2}$$

$\mathscr{H}$, in turn, is given by

$$\mathscr{H} = \mathscr{H}_S + \mathscr{H}_1 + \mathscr{H}_B . \tag{3.3}$$

$\mathscr{H}_s$ is the purely electronic and nuclear spin part of the total Hamiltonian; that is, the part of $\mathscr{H}$ which does not depend on the molecular orientation. $\mathscr{H}_B$ is the part of the total Hamiltonian which involves all the freedom degrees of the system except for the spin (electronic and nuclear) ones.[18] $\mathscr{H}_1$ denotes the interaction between these two parts. By using standard symbols,[4] we can relate our case to the following expression for $\mathscr{H}_1$:

$$\mathscr{H}_1 \equiv \sum_{p,q,\mu} (-1)^p F_\mu^{(2p)} D_{q,-p}^{(2)}(\Omega) T_\mu^{(2,q)}(\vec{\mathbf{I}},\vec{\mathbf{S}}) , \tag{3.4}$$

where μ denotes the kind of interaction involved [for example, throughout the applications of this section, Zeeman ($\mu=1$) and hyperfine interaction between electronic and nuclear moments ($\mu=2$)]. $T_\mu^{(2,q)}$ denotes the corresponding spherical tensor and the $D_{q,-p}^{(2)}(\Omega)$'s express the Wigner matrices involved in the transformation from the molecular to the laboratory framework.[4] The orientation of the molecule with respect to the laboratory frame is defined by $\Omega \equiv (\alpha,\beta,\gamma)$, where α, β, and γ are the Euler angles.

When regarding Ω as being a classical stochastic variable the time evolution of the corresponding distribution of probability, $p(\Omega;t)$, is given by

$$\frac{\partial}{\partial t} p(\Omega;t) = \Gamma(\Omega) p(\Omega;t) , \tag{3.5}$$

where, when making the diffusional assumption[19]

$$\Gamma(\Omega) \equiv -\vec{\mathbf{M}}\cdot[\overleftrightarrow{\mathbf{D}}\cdot\vec{\mathbf{M}} V(\Omega)] - \vec{\mathbf{M}}\cdot\overleftrightarrow{\mathbf{D}}\cdot\vec{\mathbf{M}} . \tag{3.6}$$

$\overleftrightarrow{\mathbf{D}}$ is the molecular diffusion tensor and $\vec{\mathbf{M}}$ is the generator of rotations. The explicit form of V to be used in this section is

$$V(\Omega) = \lambda P_2(\cos\beta) . \tag{3.7}$$

Recall that β denotes the second Euler angle and $P_2(\cos\beta)$ is the second-order Legendre polynomial.

As is well known, the SLE theory[20] consists of replacing the rigorous operator iL defined by Eq. (3.2) with the dynamical operator

$$\mathscr{L} \equiv i\mathscr{H}_S^{\times} + i\mathscr{H}_1^{\times}(\Omega) + \Gamma(\Omega) . \tag{3.8}$$

Let us consider two variables, $A(\Omega,\vec{\mathbf{I}},\vec{\mathbf{S}})$ and $B(\Omega,\vec{\mathbf{I}},\vec{\mathbf{S}})$, which, for the sake of generality, are assumed to depend on molecular orientation and nuclear and electronic angular momentum. As a consequence of replacing iL with $\mathscr{L}$ we are naturally led to define their corresponding scalar product $\langle B \mid A\rangle$ as follows:

$$\langle B \mid A\rangle \equiv \mathop{\mathrm{Tr}}_{\{S,I\}} \int d\Omega\, B(\Omega,\vec{\mathbf{I}},\vec{\mathbf{S}}) A(\Omega,\vec{\mathbf{I}},\vec{\mathbf{S}}) \rho_{\mathrm{eq}}(\vec{\mathbf{I}},\vec{\mathbf{S}}) w_{\mathrm{eq}}(\Omega) , \tag{3.9}$$

where $\rho_{\mathrm{eq}}(\vec{\mathbf{I}},\vec{\mathbf{S}})$ and $w_{\mathrm{eq}}(\Omega)$ denote the equilibrium distribution of the spin system and molecular orientation, respectively. This means that

$$\Gamma(\Omega) w_{\mathrm{eq}}(\Omega) = 0 , \tag{3.10}$$

$$w_{\mathrm{eq}}(\Omega) = \exp[-V(\beta)/kT] \Big/ \int d\Omega \exp[-V(\beta)/kT] . \tag{3.10'}$$

The correlation function $\Phi(\tau)$ of Eq. (3.1) can be written in terms of the scalar product of Eq. (3.9) as

$$\Phi(t) = \langle f_0 \mid f_0(t)\rangle / \langle f_0 \mid f_0\rangle , \tag{3.11}$$

where

$$|f_0\rangle \equiv S_+ \mathbb{1}_N . \tag{3.12}$$

$\mathbb{1}_N$ is the identity operator of the nuclear space.

We have now to face the problem of evaluating the parameters s_n. This can be done as follows. First of all, let us define the nth-order state

$$|a_n\rangle \equiv \mathscr{L}^n |f_0\rangle \ . \tag{3.13}$$

As usual in the slow-motion regime, we shall disregard the nonsecular terms. Then the general expression for $|a_n\rangle$ reads[21]

$$|a_n\rangle \equiv \sum_{l,m,i,j} [\underline{C}(n)]_{lmij} Y_{2l,m}(\Omega) \underline{A}_{ij} S_+ \ . \tag{3.14}$$

We also assumed the splitting $\overleftrightarrow{g}$, the hyperfine $\overleftrightarrow{A}$ and the diffusion $\overleftrightarrow{D}$ tensors to be axial symmetric tensors with the same symmetry axis. The nuclear-spin operators are expanded over the set of the 3×3 matrices $\underline{A}_{ij}$ defined via

$$(\underline{A}_{ij})_{lm} \equiv \delta_{il}\delta_{jm} \ , \tag{3.15}$$

$$\mathbb{1}_N = \sum_{i=1}^{3} \underline{A}_{ii} \ . \tag{3.16}$$

We are now in a position to easily teach the computer to evaluate the multidimensional array $\underline{C}(n)$, the terms of which are involved in Eq. (3.14), by the following iteration expressions:

$$\begin{aligned} |a_n\rangle &= \sum_{l,m,i,j} [\underline{C}(n)]_{lmij} Y_{2l,m}(\Omega) \underline{A}_{ij} S_+ \\ &= \sum_{l',m',i',j'} [\underline{C}(n-1)]_{l'm'i'j'} \mathscr{L} Y_{2l',m'} \underline{A}_{i'j'} S_+ \ , \end{aligned} \tag{3.17}$$

which leads to

$$[\underline{C}(n)]_{lmij} = \sum_{l',m',i',j'} R^{(lmij)}_{l'm'i'j'} [\underline{C}(n-1)]_{l'm'i'j'} \ . \tag{3.18}$$

The corresponding explicit expressions can be found in Appendix A. Symmetry constraints can significantly reduce the actual numbers of components $[\underline{C}(n)]_{lmij}$ to be evaluated (see Appendix B). The starting point of our iteration procedure is

$$[\underline{C}(0)]_{lmij} = \delta_{l0}\delta_{m0}\delta_{ij} \ . \tag{3.19}$$

The parameters s_n can then simply be obtained from

$$s_n = \langle a_0 | a_n \rangle \ . \tag{3.20}$$

By using Eq. (3.16) we arrive at

$$s_n = s_n(1) + s_n(2) + s_n(3) \ , \tag{3.21}$$

where

$$\begin{aligned} s_n(i) &= \langle S_- A_{ii} | \mathscr{L}^n | a_0 \rangle / \langle a_0 | a_0 \rangle \\ &= \operatorname*{Tr}_{\{S\}}(S_- S_+) \frac{\int d\Omega\, w_{\rm eq}(\Omega) Y_{2l,m}(\Omega) [\underline{C}(n)]_{lmji}}{3 \operatorname*{Tr}_{\{S\}}(S_- S_+) \int d\Omega\, w_{\rm eq}(\Omega)} \ . \end{aligned} \tag{3.22}$$

If we take into account that $w_{\rm eq}(\Omega)$ of Eq. (3.10′) only depends on the β-Euler angle, we can express the $s_n(i)$'s as

$$s_n(i) = \sum_l (4l+1)^{1/2} \bar{P}_{2l} [\underline{C}(n)]_{l0ii} / 3 \ , \tag{3.23}$$

where the $\bar{P}_{2l}$'s are the order parameters defined by

$$\bar{P}_{2l} \equiv \int d\Omega\, w_{\rm eq}(\Omega) P_{2l}(\cos\beta) \ . \tag{3.24}$$

$P_l(\cos\beta)$ is the lth-order Legendre polynomial. To get the results of Sec. III B these parameters were evaluated by using a suitable integration routine.[22] The numerical accuracy of this procedure was then checked by comparison with Zannoni's recursion method.[23] It was assessed that the accuracy dominion of the former method is wider than that of the latter one, where both methods are in a good agreement.

Note that Eq. (3.21) suggest the alternative approach to the EPR spectrum consisting of expressing the line shape as the summation of three continued fractions, one for each of the three contributions to the s_n's of Eq. (3.21). This means that

$$I(\omega) = \sum_{i=1}^{3} I_i(\omega) \ , \tag{3.25}$$

where $I_i(\omega)$ is the real part of the Laplace transform of the correlation function of Eq. (3.11) with the scalar product of Eq. (3.9) being replaced by

$$\begin{aligned} \langle B | A \rangle^{(i)} \equiv \sum_{\{S,I\}} \int d\Omega\, B(\Omega,\vec{I},\vec{S}) A(\Omega,\vec{I},\vec{S}) \\ \times A_{ii} \rho_{\rm eq}(\vec{I},\vec{S}) w_{\rm eq}(\Omega) \ . \end{aligned} \tag{3.26}$$

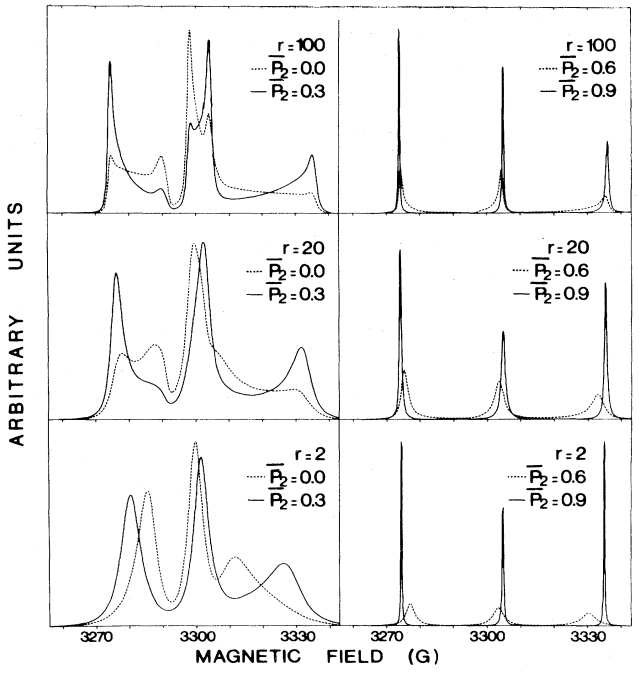

FIG. 1. Absorption spectra simulations for a nitroxide probe with axially symmetric g tensor and hyperfine tensor. $D = D_\perp = D_{||}$, $r = \frac{2}{3} |g_{||} - g_\perp| \beta H_0 / D$: β is the Bohr magneton, $H_0 = 3300G$, the static magnetic field. Magnetic parameters are $g_{||} = 2.0027$, $g_\perp = 2.0075$, $A_{||} = 32G$, and $A_\perp = 6G$. $\bar{P}_2$ is the most significant order parameter. Each pair of curves involves the same area, whereas for graphical reasons different pairs can involve different areas.

To get the results of Sec. III B we followed both methods. In the case of fairly short microscopic times we found the latter method to lead to a faster convergence. This can be accounted for as follows. In such a physical condition the spectrum consists of three well distinct line shapes, one for each continued fraction. A few steps of each continued fraction are required to clearly identify each component line shape.

B. Computational results

Figure 1 describes the results obtained by using our fast-computational algorithm in the free-diffusion case ($\bar{P}_2=0$) and in the presence of an orientating potential ($\bar{P}_2\neq 0$) for several values of the parameter r defined by

$$r\equiv\tfrac{2}{3}\,|g_{||}-g_{\perp}|\,\beta_e H_0/D\ , \tag{3.27}$$

where H_0 is the static magnetic field, β_e is the Bohr magneton, D denotes the isotropic diffusion coefficient of the spin probe under study. (The assumption of isotropy does not involve any gain in the rapidity of convergence), and $g_{||}$ and $g_{\perp}$ are the components parallel and perpendicular to the symmetry axis of the splitting tensor, respectively. In a sense, the parameter r indicates the degree of non-Markovness of our system.

Note the deep changes of the line shapes at the onset of molecular order. This effect becomes less significant as the parameter r decreases. This is in line with the widely shared opinion that the non-Markovian system is more sensitive to the details of microscopic dynamics.[20] We believe this property to especially be of relevance to study the EPR line shapes in a largely viscous system such as polymeric mesophase.

Note also that the line shapes significantly narrow as the order parameter increases. This has to be traced back to the fact that the mean squared value of the fluctuations of the local fields "felt" by the resonanting electronic spins decreases as the intensity of the orientating field increases. In Table I we report the relevant data on the computational convergence and execution times corresponding to the cases illustrated in Fig. 1.

We found it to be interesting to compare the weak diffusion region with the Redfield theory.[24] To do that we evaluated the ratio of the Redfield to the true linewidth with the parameter r ranging from $r\simeq 10^{-4}$ to 1. This was done in both the free relaxation case ($\bar{P}_2=0$) and in the presence of a strong orientating field ($\bar{P}_2=0.9$). In the explored region the former case was not found to appreciably deviate from the Redfield regime but for r close to 10^0, where deviations of a few percent appear. On the contrary, as pointed out Fig. 2, in the presence of a strong orientating field a spin probe of stearic kind is found to significantly deviate from the Redfield regime. Since the non-Markovian system (far from the Redfield regime) is most sensitive to the details of the microscopic dynamics,[20] we believe that this region could be significantly affected by corrections to the Favro equation coming from inertial effects and the nonwhite nature of the stochastic force. This would make the EPR spectroscopy a remarkable tool to test the predictions of nonlinear nonequilibrium statistical mechanics, according to which these corrections are rendered more considerable by the nonlinear nature of the orientating potentials.[25]

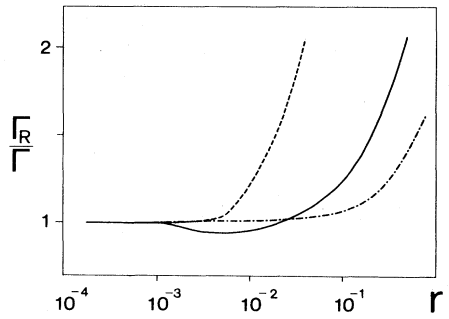

FIG. 2. Plot of the ratio between Redfield linewidth Γ_R and the exact one Γ vs $(A_{||}-A_{\perp})/D$. — — —, low field line; ——, high field line; —·—·—·, central line.

IV. CONCLUDING REMARKS

A major original feature of this paper is its completely self-contained nature. Our fast-computational algorithm is based on a theoretical foundation (physical rather than mathematical), an exhaustive account of which is given in Sec. II. None of the approaches so far attempted[7–9] seem to share this appealing characteristic of our method.

However, even at the mere level of efficiency, our approach successfully faces the challenge posed by the methods of other groups.[8] We only need 110 K bytes, [1K$\equiv 2^{10}=1024$; 1 byte$\equiv$8 bits (binary digits)], whereas 260 K bytes are required by Ref. 8. As far as the computer time is concerned (see Table I, which concerns a 600-

TABLE I. This table refers to the cases shown in Fig. 1. r is defined by Eq. (3.27), N_s is the minimum number of steps for the continued-fraction convergence to be attained, and t is the elapsed computing time in seconds.

$\bar{P}_2$	r	N_s	t	r	N_s	t	r	N_s	t
0	2	21	4.30	10	25	6.0	100	32	8.66
0.3	2	18	3.45	10	24	5.12	100	28	6.76
0.6	2	18	3.45	10	21	4.30	100	25	6.0
0.9	2	16	3.10	10	16	3.10	100	19	3.70

point spectrum), ours seems to be much shorter than that of Ref. 8 even when taking into account that their machine is about eighty times slower than our IBM 3033 machine.

APPENDIX A

In this Appendix we shall provide explicit expressions for the recursion formulas of Eq. (3.18). To this aim we need these preliminary definitions:

$$
\begin{aligned}
&A \equiv i(A_{||}+2A_{\perp})/3 ,\\
&B \equiv i\tfrac{2}{3}(g_{||}-g_{\perp})\beta_e H ,\\
&C \equiv i(A_{||}-A_{\perp}) ,\\
&D \equiv (\tfrac{3}{16})^{1/2} C ,
\end{aligned}
\tag{A1}
$$

$$
\begin{aligned}
&C_M \equiv \int d\cos\theta\, d\phi\, Y^*_{l,m}(\theta,\phi)\Gamma^+ Y_{l-2,m}(\theta,\phi) ,\\
&C_0 \equiv \int d\cos\theta\, d\phi\, Y^*_{l,m}(\theta,\phi)\Gamma^+ Y_{l,m}(\theta,\phi) ,\\
&C_P \equiv \int d\cos\theta\, d\phi\, Y^*_{l,m}(\theta,\phi)\Gamma^+ Y_{l+2,m}(\theta,\phi) ,
\end{aligned}
\tag{A2}
$$

$$
\begin{aligned}
&C_{10} \equiv C(l,2,l,m-1,1)C(l,2,l,0,0) ,\\
&C_{1M} \equiv C(l+2,2,l,m-1,1)C(l+2,2,l,0,0)\{[2(l+2)+1]/[2l+1]\}^{1/2} ,\\
&C_{1P} \equiv C(l-2,2,l,m-1,1)C(l-2,2,l,0,0)\{[2(l-2)+1]/[2l+1]\}^{1/2} ,\\
&C_{00} \equiv C(l,2,l,m,0)C(l,2,l,0,0) ,\\
&C_{0M} \equiv C(l+2,2,l,m,0)C(l+2,2,l,0,0)\{[2(l+2)+1]/[2l+1]\}^{1/2} ,\\
&C_{0P} \equiv C(l-2,2,l,m,0)C(l-2,2,l,0,0)\{[2(l-2)+1]/[2l+1]\}^{1/2} ,\\
&C_{M10} \equiv C(l,2,l,m+1,-1)C(l,2,l,0,0) ,\\
&C_{M1M} \equiv C(l+2,2,l,m+1,-1)C(l+2,2,l,0,0)\{[2(l+2)+1]/[2l+1]\}^{1/2} ,\\
&C_{M1P} \equiv C(l-2,2,l,m+1,-1)C(l-2,2,l,0,0)\{[2(l-2)+1]/[2l+1]\}^{1/2} .
\end{aligned}
\tag{A3}
$$

β_e is the Bohr magneton, $i=\sqrt{-1}$, H_0 is the magnetic field. The symbol $Y_{l,m}(\theta,\phi)$ denotes the spherical harmonics. We follow, furthermore, Rose's notation,[26] according to which $C(l,l',l'',m,m')$ denotes the Clebsch-Gordan coefficients. Note that the quantities defined by (A2) and (A3) refer to the same (generic) pair of the indices l and m and are independent of i and j.

We are now in a position to give the relationships connecting the $[\underline{C}(n)]_{lmij}$'s [here renamed $\overline{W}(l,m,i,j)$] to the $[\underline{C}(n-1)]_{lmij}$'s [here renamed $W(l,m,i,j)$]. When exploring all the pairs of indices i and j we get

$$
\begin{aligned}
\overline{W}(l,m,1,1)=&[W(l+2,m+1,2,1)C_{M1M}+W(l,m+1,2,1)C_{M10}+W(l-2,m+1,2,1)C_{M1P}]D\\
&+[W(l+2,m-1,1,2)C_{1M}+W(l,m-1,1,2)C_{10}+W(l-2,m-1,1,2)C_{1P}](-D)\\
&+2W(l+2,m,1,1)[(C/2+B)C_{0M}+C_P]+2W(l,m,1,1)[(C/2+B)C_{00}-A/2+C_0]\\
&+2W(l-2,m,1,1)[(C/2+B)C_{0P}+C_M] ,\\
\overline{W}(l,m,1,2)=&\{[W(l+2,m+1,2,2)+W(l+2,m+1,1,1)]C_{M1M}+[W(l,m+1,2,2)+W(l,m+1,1,1)]C_{M10}\\
&+[W(l-2,m+1,2,2)+W(l-2,m+1,1,1)]C_{M1P}\}D\\
&+[W(l+2,m-1,1,3)C_{1M}+W(l,m-1,1,3)C_{10}+W(l-2,m-1,1,3)C_{1P}](-D)\\
&+W(l-2,m,1,2)[(2B+C/2)C_{0P}+2C_M]+W(l,m,1,2)[(2B+C/2)C_{00}-A/2+2C_0]\\
&+W(l+2,m,1,2)[(2B+C/2)C_{0M}+2C_P] ,\\
\overline{W}(l,m,1,3)=&\{[W(l+2,m+1,1,2)+W(l+2,m+1,2,3)]C_{M1M}+[W(l,m+1,1,2)+W(l,m+1,2,3)]C_{M10}\\
&+[W(l-2,m+1,1,2)+W(l-2,m+1,2,3)]C_{M1P}\}D+W(l-2,m,1,3)(2BC_{0P}+2C_M)
\end{aligned}
$$

$$+W(l,m,1,3)(2BC_{00}+2C_0)+W(l+2,m,1,3)(2BC_{0M}+2C_P)\ ,$$

$$\overline{W}(l,m,2,1)=[W(l+2,m+1,3,1)C_{M1M}+W(l,m+1,3,1)C_{M10}+W(l-2,m+1,3,1)C_{M1P}]D$$
$$+\{[W(l+2,m-1,2,2)+W(l+2,m-1,1,1)]C_{1M}+[W(l,m-1,2,2)+W(l,m-1,1,1)]C_{10}$$
$$+[W(l-2,m-1,2,2)+W(l-2,m-1,1,1)]C_{1P}\}(-D)$$
$$+W(l-2,m,2,1)[(2B+C/2)C_{0P}+2C_M]+W(l,m,2,1)[(2B+C/2)C_{00}-A/2+2C_0]$$
$$+W(l+2,m,2,1)[(2B+C/2)C_{0M}+2C_P]\ ,$$

$$\overline{W}(l,m,2,2)=\{[W(l+2,m+1,3,2)+W(l+2,m+1,2,1)]C_{M1M}+[W(l,m+1,3,2)+W(l,m+1,2,1)]C_{M10}$$
$$+[W(l-2,m+1,3,2)+W(l-2,m+1,2,1)]C_{M1P}\}D$$
$$+\{[W(l+2,m-1,2,3)+W(l+2,m-1,1,2)]C_{1M}+[W(l,m-1,2,3)+W(l,m-1,1,2)]C_{10}$$
$$+[W(l-2,m-1,2,3)+W(l-2,m-1,1,2)]C_{1P}\}(-D)+2W(l-2,m,2,2)(BC_{0P}+C_M)$$
$$+2W(l,m,2,2)(BC_{00}+C_0)+2W(l+2,m,2,2)(BC_{0M}+C_P)\ ,$$

$$\overline{W}(l,m,2,3)=\{[W(l+2,m+1,3,3)+W(l+2,m+1,2,2)]C_{M1M}+[W(l,m+1,3,3)+W(l,m+1,2,2)]C_{M10}$$
$$+[W(l-2,m+1,3,3)+W(l-2,m+1,2,2)]C_{M1P}\}D$$
$$+[W(l+2,m-1,1,3)C_{1M}+W(l,m-1,1,3)C_{10}+W(l-2,m-1,1,3)C_{1P}](-D)$$
$$+W(l-2,m,2,3)[(2B-C/2)C_{0P}+2C_M]+W(l,m,2,3)[(2B-C/2)C_{00}+A/2+2C_0]$$
$$+W(l+2,m,2,3)[(2B-C/2)C_{0M}+2C_P]\ ,$$

$$\overline{W}(l,m,3,1)=\{[W(l+2,m-1,2,1)+W(l+2,m-1,3,2)]C_{1M}+[W(l,m-1,2,1)+W(l,m-1,3,2)]C_{10}$$
$$+[W(l-2,m-1,2,1)+W(l-2,m-1,3,2)]C_{1P}\}(-D)+2W(l-2,m,3,1)(BC_{0P}+C_M)$$
$$+2W(l,m,3,1)(BC_{00}+C_0)+2W(l+2,m,3,1)(BC_{0M}+C_P)\ ,$$

$$\overline{W}(l,m,3,2)=[W(l+2,m+1,3,1)C_{M1M}+W(l,m+1,3,1)C_{M10}+W(l-2,m+1,3,1)C_{M1P}]D$$
$$+\{[W(l+2,m-1,2,2)+W(l+2,m-1,3,3)]C_{1M}+[W(l,m-1,2,2)+W(l,m-1,3,3)]C_{10}$$
$$+[W(l-2,m-1,2,2)+W(l-2,m-1,3,3)]C_{1P}\}(-D)$$
$$+W(l-2,m,3,2)[(2B-C/2)C_{0P}+2C_M]+W(l,m,3,2)[(2B-C/2)C_{00}+A/2+2C_0]$$
$$+W(l+2,m,3,2)[(2B-C/2)C_{0M}+2C_P]\ ,$$

$$\overline{W}(l,m,3,3)=[W(l+2,m+1,3,2)C_{M1M}+W(l,m+1,3,2)C_{M10}+W(l-2,m+1,3,2)C_{M1P}]D$$
$$+[W(l+2,m-1,2,3)C_{1M}+W(l,m-1,2,3)C_{10}+W(l-2,m-1,2,3)C_{1P}](-D)$$
$$+W(l-2,m,3,3)[(2B-C)C_{0P}+2C_M]+W(l,m,3,3)[(2B-C)C_{00}+A+2C_0]$$
$$+W(l+2,m,3,3)[(2B-C)C_{0M}+2C_P]\ .$$

APPENDIX B

As stressed in Sec. III A, a basic step of our approach is to determine

$$\mathscr{L}^n S_+=\sum_{l,m,i,j}[\underline{C}(n)]_{lmij}Y_{2l,m}(\Omega)A_{ij}S_+ \tag{B1}$$

[see Eq. (3.17)]. For a fixed value of n, the index l explores all the even values ranging from 0 to $2n$ and m should range from l to $-l$ thereby making the dimensions of $\underline{C}(n)$ overwhelming.

However, it is possible to show the following.

(i) m ranges from -2 to 2. This can be arrived at by remarking that the index m is made to change by the terms $Y_{2-1}I_+$ and $Y_{21}I_-$ of the equation in Ref. 21 and $(I_+)^3=(I_-)^3=0$ $(I=1)$.

(ii) $[\underline{C}(n)]_{lmij}=(-1)^m[\underline{C}(n)]_{l-mji}$. This useful relationship can be obtained by using the operator $\underline{T}$ defined as follows:

$$\underline{T}\equiv\underline{K}\,\underline{P}\,\underline{\mathbb{1}}_s\ , \tag{B2}$$

where

$$\underline{K}Y_{2l,m}(\Omega)\equiv(-1)^m Y_{2l,-m}(\Omega)\ , \tag{B3}$$

$$\underline{P}A_{ij}\equiv A_{ji}\ , \tag{B4}$$

and 1_s is the identity operator of the electronic spin space. Since $\mathscr{H}_s=\mathscr{H}_s^{\dagger}$, $\underline{T}$ commutes with $\mathscr{H}_s$. This leads us to

$$\underline{T}(\mathscr{L}^n S_+)\underline{T}^{-1}=\mathscr{L}^n\underline{T}S_+\underline{T}^{-1}=\mathscr{L}^n S_+\ . \tag{B5}$$

On the other hand, by applying this transformation to the right-hand side (rhs) of Eq. (B1)

$$\sum_{i,j,l,m}[\underline{C}(n)]_{lmij}\underline{T}[A_{ij}Y_{2l,m}(\Omega)S_+]\underline{T}^{-1}=\sum_{i,j,l,m}[\underline{C}(n)]_{lmij}A_{ji}(-1)^m Y_{2l,-m}(\Omega)S_+$$
$$=\sum_{i,j,l,m}[\underline{C}(n)]_{lmij}A_{ij}Y_{2l,m}(\Omega)S_+\ . \tag{B6}$$

From Eqs. (B6), (B5), and (B1) we obtain the useful property (ii).

As a consequence the only independent terms to be determined are $C_{l011}(n)$, $C_{l022}(n)$, $C_{l033}(n)$, $C_{l123}(n)$, $C_{l112}(n)$, and $C_{l213}(n)$.

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$$\mathscr{H}_s+\mathscr{H}_1=\tfrac{1}{3}[(g_{||}+2g_{\perp})\beta_e H_0 S_z+(A_{||}+2A_{\perp})S_z I_z]$$
$$+\tfrac{2}{3}D^{(2)}_{00}(\Omega)[(A_{||}-A_{\perp})I_z+(g_{||}-g_{\perp})\beta_e H_0]S_z$$
$$-(\tfrac{1}{6})^{1/2}(A_{||}-A_{\perp})[D^{(2)}_{10}(\Omega)I_+-D^{(2)}_{-10}(\Omega)I_-]S_z\ ,$$

where β_e is the bohr magneton. The general form of Eq. (3.14) is justified by the fact that no S_+ and S_- appear and $[S_z,S_+]=S_+$.
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