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General treatment of paramagnetic relaxation enhancement associated with translational diffusion

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A theory of nuclear spin relaxation in isotropic liquids for nuclear spins interacting with electron spins, residing in other molecules (the outer-sphere relaxation), is presented. The approach, valid outside of the Redfield limit for electron spin relaxation, is an extension of the Swedish slow motion theory [Benetis et al., Mol. Phys. 48, 329 (1983); Nilsson and Kowalewski, J. Magn. Reson. 146, 345 (2000)] for inner-sphere relaxation. It is demonstrated that the outer-sphere relaxation rate can be expressed as an integral of a product of a translational diffusion correlation function and a function analogous to the inner-sphere spectral density. A numerical implementation of the theory is described and applied to a large number of realistic parameter sets for $S = 7/2$ and $S = 1$, which may correspond to Gd(III) and Ni(II) systems. It is shown that the outer-sphere contribution is relevant and should be included into the analysis of nuclear magnetic relaxation dispersion relaxation profiles, especially for slow relative translational diffusion and fast molecular tumbling.

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I. INTRODUCTION

Studies of NMR spin-lattice relaxation rates as a function of the magnetic field [nuclear magnetic relaxation dispersion (NMRD)] in solutions of paramagnetic ions or complexes have for long time attracted considerable attention.\textsuperscript{1-3} The paramagnetic species cause an increase of spin-lattice relaxation rate for the nuclear spins (usually protons), denoted commonly as paramagnetic relaxation enhancement (PRE). The field dependence of the PRE carries potentially a wealth of information on structure and dynamics of the species involved, provided that appropriate theoretical models are available. PRE/NMRD measurements are commonly carried out for spins belonging to the solvent molecules (most often water).

One usually considers the measured PRE as consisting of two contributions, referred to as the inner-sphere and the outer-sphere parts. The inner-sphere contribution comes from the nuclear spin residing in molecules entering the first coordination shell of the metal ion, while the molecules outside of this shell contribute to the outer-sphere part. For the inner-sphere contribution, one assumes usually that the effective distance between the spins is constant, while this obviously is not the case for the outer-sphere mechanism. Some authors use also the concept of the second-shell PRE, with a mechanism similar to the inner-shell contribution, arising from a discrete number of solvent molecules in a well-defined second solvation sphere.\textsuperscript{4}

The early theory of the inner-sphere PRE is known as the Solomon–Bloembergen–Morgan (SBM) theory.\textsuperscript{1-3} Shortcomings of the SBM approach are well known, but the issue of more advanced modeling of the PRE has long been recognized as difficult.\textsuperscript{5} It seems now that some of the fundamental problems have been solved. In a recent study, three formalisms proposed in literature were compared to each other\textsuperscript{6} and it was found that two of them agreed very closely, in spite of large differences in the mathematical treatment, and that the discrepancies with the third one can be explained by an approximate description of the electronic spin relaxation. This obviously increases the credibility of these methods.

The objective of this communication is to present how an approach similar to the general inner-sphere formalism developed in our laboratory\textsuperscript{5,12} can be applied to the outer-sphere PRE. A “classical” way of dealing with the outer-sphere issue can be found in Abragam’s treatise\textsuperscript{13} and in the works by Torrey\textsuperscript{14} and Pfeifer.\textsuperscript{15} In an important paper by Hwang and Freed,\textsuperscript{16} some mathematical mistakes of the earlier work were corrected and the role of the intermolecular forces, as reflected in the radial distribution functions (rdfs), was incorporated in the theory. A very similar approach was proposed, independently, by Ayant et al.\textsuperscript{17} A simple but important special case, denoted as force-free diffusion, arises in these treatments if the rdf is considered flat from the distance of closest approach to infinity. Ayant et al.\textsuperscript{17} also considered the effect of translation-rotation coupling\textsuperscript{18} while Freed extended the Hwang–Freed model by including, in a very simple way, the electron spin relaxation effects.\textsuperscript{19} The resulting model can be considered as the outer-sphere counterpart of the SBM theory. More careful treatment of electron spin relaxation, valid within the Redfield limit,\textsuperscript{20} and its effect on the outer-sphere PRE was proposed by Kruk et al.\textsuperscript{21,22} The second of these studies deals, on the equal level, with the inner-sphere case.\textsuperscript{23} Related work was also proposed by
Sharp and co-workers\textsuperscript{23-25} and by Rast and co-workers.\textsuperscript{26,27} While the effects of the structure of the rdf can be included at this level\textsuperscript{28-31} we limit our interest here to the force-free diffusion and concentrate on the difficulties caused by the complexity of electron spin relaxation outside of the Redfield limit.\textsuperscript{7-12,32-36} In this way, we bring the outer-sphere PRE theory to the same level as the inner-sphere version.\textsuperscript{6,12}

The outline of this paper is as follows. In Sec. II, we review some basic concepts of the “Swedish slow motion theory” in general. This is followed by the presentation of the outer-sphere PRE theory (Sec. III) and of computational details (Sec. IV). Illustrative numerical examples are presented and discussed in Sec. V and conclusions are drawn in Sec. VI.

II. REVIEW OF BASIC CONCEPTS OF THE SWEDISH SLOW MOTION THEORY

The Swedish slow motion theory has been developed to interpret nuclear (proton) relaxation profiles for paramagnetic systems for arbitrary motional conditions and interaction strengths characterizing the electron spin, beyond validity regimes of time-dependent perturbation approaches. The name “slow motion” refers to situations when the motion modulating the relevant spin interactions is so slow, compared to the time scale of the spin dynamics, that the perturbation theory of the electron spin relaxation breaks down. In this section, we shall outline the underlying assumptions and motional models incorporated into this treatment.

For transition metal complexes with $S \geq 1$, the electron spin manifold is split due to the indirect interaction between unpaired electrons through the spin-orbit coupling. The zero field splitting (ZFS) Hamiltonian $H_{\text{ZFS}}(t)$ can be expressed as a sum of two components: $H_{\text{ZFS}}(t) = (H_{\text{ZFS}}(t)) + (H(t) - (H_{\text{ZFS}}(t))) = H_{\text{ZFS}}^S + H_{\text{ZFS}}^T(t)$. The decomposition of the total Hamiltonian is performed in a molecular frame, i.e., in any coordinate system fixed in the molecule. The first term represents an averaged part of the ZFS interaction, referred to in the literature as the static (permanent) ZFS, $H_{\text{ZFS}}^S$, while the second one describes stochastic fluctuations of the ZFS Hamiltonian around this averaged value and is called transient ZFS, $H_{\text{ZFS}}^T(t)$. The principal frame of the static ZFS ($P_S$) can change its orientation with respect to the laboratory axis systems ($L$) due to overall, isotropic molecular tumbling. This implies that the $H_{\text{ZFS}}^S$ Hamiltonian takes in the laboratory frame the form

$$H_{\text{ZFS}}^{(L)} = \sqrt{\frac{2}{3}} D_3 \sum_{m=-2}^{2} (-1)^m \left( \sum_{k=-2}^{2} V^{2,(P)} \langle D_{k,m}^{2}(\Omega_{P,L}) \rangle \right) T_{2,m}^{S}(S),$$

where $V^{2,(P)} = 1$, $V_{1}^{2,(P)} = 0$, $V_{-1}^{2,(P)} = (4/\sqrt{6})(E_{\text{ps}}/D_{3})$. The quantities $D_3$ and $E_{\text{ps}}$ describe the axial and rhombic components of the static (rank-2) ZFS tensor, respectively, while the relative orientation of the ($P_S$) and ($L$) frames is described by the angle $\Omega_{P,L}(t)$. The operators $T_{m}^{S}(S)$ are $T_{0}^{S}(S) = (1/\sqrt{6})[3 S^2 S(S+1)]$, $T_{1}^{S}(S) = (1/2)[S S_{z} + S_{z} S_{z}]$, and $T_{2}^{S}(S) = 1/2 S_{z}^2$.

Higher-order ZFS terms can exist for spin systems with $S > 3/2$. They were discussed in the relaxation context by Rast et al\textsuperscript{37,38} and by Sharp and co-worker.\textsuperscript{39,40} While possibly important, these terms are not included in the present work since they are not judged necessary to reach the main objective of the present study: to estimate the relative importance of the outer-sphere and inner-sphere relaxivity components outside of the Redfield limit for the electron spin relaxation.

The spread of the ZFS interaction, i.e., its transient part, is caused by stochastic fluctuations of the ligand framework. The form of the transient ZFS Hamiltonian depends on the motional model applied to describe the fluctuations. The simplest possible model assumes that the transient ZFS has a constant magnitude and a principal direction [a principal axis system $(P_T)$]. The $(P_T)$ frame changes its orientation relative to the $(P_S)$ frame according to the isotropic rotational diffusion equation with the rank-two correlation time $T_D$. Since the fluctuations of the ligand framework occur due to distortional (vibrational) dynamics of the complex, this time constant is called a distortional (vibrational) correlation time. This model is referred to in literature as the “pseudorotational model.”\textsuperscript{41} Thus, by analogy with the static ZFS interaction, the Hamiltonian $H_{\text{ZFS}}^{T(P)}$, written in the laboratory axis system, takes the form

$$H_{\text{ZFS}}^{T(L)}(S) = \sqrt{\frac{2}{3}} D_T \sum_{m=-2}^{2} (-1)^m \left( \sum_{k=-2}^{2} A^{2,(P)}(\Omega_{P,L}) D_{k,m}^{2}(\Omega_{P_T}) \right) \times D_{m,-m}^{2}(\Omega_{P,L}) T_{2,m}^{S}(S),$$

with $A_{k}^{2,(P)} = 1$, $A_{\pm 1}^{2,(P)} = 0$, $A_{\pm 2}^{2,(P)} = (4/\sqrt{6})(E_{\text{ps}}/D_{3})$, where $D_T$ and $E_T$ are the transient counterparts of $D_3$ and $E_{\text{ps}}$ parameters. The first transformation in Eq. (2) is between the $(P_T)$ and $(P_S)$ frames via the Euler angle $\Omega_{P,S}(t)$ modulated by the molecular tumbling (characterized by a rank-two rotational correlation time $T_R$). The representations of the static and transient ZFS, given by Eqs. (1) and (2), respectively, are included in the “slow motion theory.” In the case of inner-sphere relaxation, the I-S dipole-dipole axis defines the molecular frame ($M$) for the complex. The relative orientation of the $(P_S)$ and $(M)$ frames is described by an angle denoted as $\Omega_{P,M}$.

Referring to the applied models of the spin interactions and their fluctuations, one can now specify more explicitly the possible situations when the perturbation approach does not apply to the electron spin dynamics. The relationship between the static ZFS, $H_{\text{ZFS}}$, and the rotational correlation time, $T_R$, can bring the electron spin outside the validity range of the perturbation treatment, which requires an unambiguous decomposition of the entire spin Hamiltonian into a main part (determining the energy level structure of the system) and a perturbing part (causing transition between the energy levels, i.e., relaxation). This means that for $[H_{\text{ZFS}}^{S} T_R]$...
PRE associated with translational diffusion


\( \ll 1 \), the static ZFS acts as a relaxation mechanism, for \( |H_{ZFS}^2 \tau_0| \gg 1 \) it contributes to the electron spin energy level structure, while in the intermediate regime the perturbation treatment breaks down. Since the distortional correlation time is very short (of the order of picoseconds) the condition \( |H_{ZFS}^2 \tau_0| \ll 1 \) is usually fulfilled. Nevertheless, there can be some exceptions, i.e., for complexes with very large transient ZFS. Actually, if \( H_{ZFS}^T > H_{ZFS}^e \) (especially if the static ZFS vanishes due to high symmetry of the complex), the electron spin is at low field locked in the \((P_f)\) frame instead of the \((L)\) frame, i.e., its energy level structure is determined by the transient (rather than static) ZFS. Since, contrary to the static ZFS, the \((P_f)\) frame is not fixed in the molecule (it fluctuates very fast with the correlation time \( \tau_0 \)), the transient ZFS does not provide a stationary basis set and the perturbation theory does not apply in this case.\(^{2,5,42}\)

Even though the electron spin subsystem is beyond the validity range of the perturbation treatment, the nuclear spin relaxation can be treated in this way and expressed as a quantity proportional to a quantum-mechanical spectral density \( K_{1,1}^{DD} (-\omega) \), including the electron spin dynamics. Electron spin relaxation rates, present in the SBM theory, cannot be defined in this regime. The main reason of the general, slow motion theory is to evaluate the spectral density \( K_{1,1}^{(DD)} (-\omega) \) without invoking the electron spin relaxation rates. Instead, it is evaluated by defining an infinite and complete, orthonormal basis \( \{|O\}_i \)\(^{2,5}\) including all relevant degrees of freedom and expressing all components of the spin interactions and dynamics (the corresponding Liouville operators) in this basis, by applying the Wigner–Eckart theorem. The properties of the general theory make it possible to adapt it to various systems, when any simplified treatments break down. However, the theory is rather demanding from the computational point of view. The main reasons for computational complexity are the classical stochastic processes, i.e., the rotational and distortional degrees of freedom. Their classical nature requires setting up, in principle, an infinite basis representing the continuum of rotational and distortional states. The theory can also be applied together with a more sophisticated treatment of the distortions of the solvation shell\(^{43-45}\) instead of the pseudorotation model, but this increases the computational costs even further.

This approach has so far been applied to the inner-sphere nuclear spin relaxation. In Sec. III we let it include the translational degrees of freedom and formulate an analogous description of the outer-sphere nuclear spin relaxation, to complete the theory of nuclear spin relaxation for paramagnetic systems. The approach can be called general, referring to its validity outside of the Redfield regime, but is within limits of the applied assumptions, not least concerning the form of the ZFS Hamiltonian and the pseudorotation model.

III. THEORY OF OUTER-SPHERE PARAMAGNETIC RELAXATION ENHANCEMENT

In this section, we present a formal mathematical description of the outer-sphere PRE. We shall keep very close analogy to the description of the inner-sphere PRE given in the literature.\(^{5,12,22}\) We intend to underline in this way the unity of the general approach and make a comparison of the inner- and outer-sphere descriptions straightforward. Thus, we begin with the usual form of the quantum-mechanical spectral density, \( K_{1,1}^{(DD)} (-\omega) \):

\[
K_{1,1}^{(DD)} (-\omega) = \int_0^\infty \text{Tr}_L [\hat{T}_i^{(DD)}(\tau) \exp(-i\hat{\Omega}_{ML}^L(\tau)\hat{\rho}_L^L)] 
\times \exp(-i\omega \tau) d\tau.
\]

(3)

For the inner-sphere case, the spin-lattice relaxation rate for a nuclear spin in the paramagnetic complex is given by \( R_1 = 2 \text{ Re}[K_{1,1}^{(DD)} (-\omega)] \).\(^{5,12,22}\) In the outer-sphere case, the situation is similar but the tensor operators \( T_i^{(DD,Diff)} \) are defined as

\[
T_i^{(DD,Diff)} = \sqrt{30} \sum_{q=1}^1 \left( \begin{array}{ccc} 2 & 1 & 1 \\ 1-q & q & -1 \end{array} \right) \times S_q^0 D_{0,1-q}^{\Delta}(\Omega_{DDL}).
\]

(4)

The notation \( T_i^{(DD,Diff)} \) is introduced to refer explicitly to the translational diffusion modulating the nuclear spin \((I)\)—electron spin \((S)\) dipole–dipole interaction. The original expression for the tensor operator \( T_i^{(DD)} = C_{DD} \sum_{q=1}^1 \left( \begin{array}{ccc} 2 & 1 & 1 \\ 1-q & q & -1 \end{array} \right) S_q^0 D_{0,1-q}^{\Delta}(\Omega_{DDL}) \), where \( C_{DD} = (\mu_0/4\pi)(\gamma_I^2 \gamma_S^2 / r_{IS}^2) \) is the dipole–dipole coupling constant [see, for example, Eq. (32) of Ref. 5], has in Eq. (4) been rewritten using the form of \( T_i^{(DD,Diff)} \), which is more suitable for the outer-sphere calculations. The relative orientation of the \( I-S \) dipole–dipole and laboratory axes, described by the Wigner rotation matrices \( D_{0,1-q}^{\Delta}(\Omega_{DDL}) \), is modulated in the present case by translational diffusion. It should be noted that, due to the translational motion, the dipole–dipole axis is no longer fixed in the molecule and cannot therefore be treated as a molecular axis. For that reason, Eq. (4) contains the Wigner rotation matrices \( D_{0,1-q}^{\Delta}(\Omega_{DDL}) \) instead of \( D_{0,1-q}^{\Delta}(\Omega_{ML}) \) (\( M \) denotes a molecular frame), used in the inner-sphere case.\(^{5,11,22}\) This essential difference is illustrated in Fig. 1. Since the translational motion changes also the
interspin distance $r_{IS}$, the concept of the dipole-dipole coupling constant is not useful and the $r_{IS}^3$ factor is in Eq. (4) combined with $D_{0,1,\rho}(\Omega_{DDL})$. The lattice Liouville operator $\hat{L}_L$ contains now, besides the terms relevant for the inner-sphere relaxation,\textsuperscript{2,5,11,22} the Liouvillian, $\hat{L}_{Diff}$, representing the translational diffusion:

$$\hat{L}_{Diff} = -i D_{Diff} \nabla_{IS}^2$$

(6)

where the index $r_{IS}$ indicates that the differential operator $\nabla_{IS}^2$ contains terms related to changes of the interspin distance, as well as of the orientation of the dipole-dipole axis [i.e., $\nabla_{IS}^2 = (\Omega_{DDL})$]. The other terms describe, respectively: Zeeman interaction for the electron spin, $\hat{L}_Z(S)$, the static and transient parts of the ZFS interactions, $\hat{L}_Z$ and $\hat{L}_T$, the distortional motion, $\hat{L}_D$, and the molecular tumbling, $\hat{L}_T$. By substituting the tensor operators of Eq. (4) into Eq. (3), we obtain the “outer-sphere” counterpart of the quantum-mechanical spectral density, $K_{1,1,Diff}(\omega_0)$ which we denote $K_{1,1,Diff}^{DD,Diff}(\omega_0)$:

$$K_{1,1,Diff}^{DD,Diff}(\omega_0) = 30 \left( \frac{\mu_0}{4 \pi} \gamma_1 \gamma_3 \right)^2 \frac{1}{2 S + 1} \sum_{p,q=1} \left( \begin{array}{ccc} 2 & 1 & 1 \\ 1-p & p & -1 \end{array} \right) \times \left( \begin{array}{ccc} 1 & 1 & 1 \\ -1 & q & -1 \end{array} \right) \right)^\infty \int_0 \left\{ \begin{array}{l} Tr_{L}(S_p^{1+} D_{0,1,\rho}(\Omega_{DDL})^{1+} S_q^{1+}) \\ \exp(-i \hat{L}_{Diff}(\omega_0) d\tau) \end{array} \right\}$$

(7)

where the term $1/(2S+1)$ is the equilibrium density operator, $\rho_{eq}$, in the high temperature approximation. To proceed further with the calculations, it is highly advantageous to analyze dependencies (correlations) between different processes contributing to the lattice dynamics, represented by the operator $\hat{L}_L$ [Eq. (5)]. Formally, a part corresponding to a certain degree of freedom can be factored out from the general quantum-mechanical correlation function if it is independent of the remaining contributions to the lattice dynamics. Since the translational diffusion affects neither the electron spin dynamics nor the molecular tumbling,\textsuperscript{2,5,21} we shall extract the translational correlation function

$$C_{Diff}^{DD,Diff}(\tau) = \int_{\omega_0} \left\{ \begin{array}{l} D_{0,1,\rho}(\Omega_{DDL})^{1+} S_q^{1+} \\ \exp(-i \hat{L}_{Diff}(\omega_0) d\tau) \end{array} \right\}$$

(8)

from the total correlation function of Eq. (7):

$$K_{1,1,Diff}^{DD,Diff}(\omega_0) = 30 \left( \frac{\mu_0}{4 \pi} \gamma_1 \gamma_3 \right)^2 \frac{1}{2 S + 1} \sum_{p,q=1} \left( \begin{array}{ccc} 2 & 1 & 1 \\ 1-p & p & -1 \end{array} \right) \times \left( \begin{array}{ccc} 1 & 1 & 1 \\ -1 & q & -1 \end{array} \right) \right)^\infty \int_0 \left\{ \begin{array}{l} Tr_{L}(S_p^{1+} D_{0,1,\rho}(\Omega_{DDL})^{1+} S_q^{1+}) \\ \exp(-i \hat{L}_{Diff}(\omega_0) d\tau) \end{array} \right\}$$

(9)

The operator $\hat{L}_{Diff}$ contains all contributions present in Eq. (5) except $\hat{L}_{Diff}$, i.e., $\hat{L}_{Diff} = \hat{L}_Z(S) + \hat{L}_T(S) + \hat{L}_D + \hat{L}_R$. Hence, the operator $\hat{L}_{Diff}$ is identical with the lattice Liouvillian containing the degrees of freedom that are relevant for the inner-sphere calculations, i.e., the electron spin interactions, the distortional motion, and the rotational motion. In fact, the decomposition performed in Eq. (9) is necessary to carry out the final numerical calculations; the computational complexity would otherwise be too high. For a force-free diffusion with a uniform distribution of the solvent molecules outside the distance of closest approach, $d$, and under the assumption of the reflecting wall boundary condition at $r_{IS}=d$, the correlation function for translational diffusion takes the form\textsuperscript{16,17}

$$C_{Diff}^{DD,Diff} = C_{Diff}(\tau) = \frac{72}{5 \cdot d^2} N_S \int_0 \left[ \begin{array}{l} \frac{u^2}{81 + 9u^2 - 2u^4 + u^6} \\ \exp(- \frac{D_{Diff}}{d^2} \tau) \end{array} \right] du,$$

(10)

where $N_S$ is the number of spins $S$ per unit volume, while $D_{Diff}$ is the relative (mutual) translational diffusion coefficient of the molecules carrying the spins $I$ and $S$, and is defined as a sum of the diffusion coefficients of these molecules. This form of the correlation function has been used for the calculations of the outer-sphere PRE when the electron spin subsystem satisfies the conditions of the Redfield relaxation theory.\textsuperscript{21,22} and we shall use it in the general case as well. This form of the translational correlation function leads, when substituted into Eq. (9), to the following expression for the spectral density, $K_{1,1,Diff}^{DD,Diff}(\omega_0)$:

$$K_{1,1,Diff}^{DD,Diff}(\omega_0) = 30 \left( \frac{\mu_0}{4 \pi} \gamma_1 \gamma_3 \right)^2 \frac{1}{2 S + 1} \sum_{p,q=1} \left( \begin{array}{ccc} 2 & 1 & 1 \\ 1-p & p & -1 \end{array} \right) \times \left( \begin{array}{ccc} 1 & 1 & 1 \\ -1 & q & -1 \end{array} \right) \right)^\infty \int_0 \left[ \begin{array}{l} \frac{u^2}{81 + 9u^2 - 2u^4 + u^6} \\ \exp(- \frac{D_{Diff}}{d^2} \tau) \end{array} \right] du,$$

(11)

In this equation, we have interchanged the order of integration, integrating first over time, and included the terms
-\left(D_{\text{Diff}}/d^2\right)u^2 \tau \text{ and } -i\omega_1 \tau\) into the exponential. One can see from Eq. (11) that the calculations of the spectral density \(\tilde{K}_{1,1,\text{Diff}}(-\omega)\) can be performed in two steps. The first step is to evaluate the “internal” spectral density:

\[
\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega) = \sum_{p,q=1}^{1} \left( \begin{array}{ccc} 2 & 1 & 1 \\ 0 & p & -1 \\ 1 & q & -1 \end{array} \right) \int_0^\infty \text{Tr}(\tilde{K}^{\text{Diff}}(u, -\omega)) d\tau,
\]

which is dependent on the \(u\) variable. In the next step, one has to perform the integration:

\[
K_{1,1,\text{Diff}}^{\text{DD}}(-\omega) = 30 \left( \frac{\mu_0 \hbar \gamma_i \gamma_j}{4\pi} \right)^2 \frac{72}{2S+1} 5^2 \left\langle S^2 \right\rangle_{\text{NS}}
\]

\[
\times \int_0^\infty \left( \frac{u^2}{81+9u^2-2u^4+u^6} \right)^{\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega)} du,
\]

The spectral density \(\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega)\) can be evaluated by following the strategy of the inner-sphere calculations. The translational degrees of freedom have been separated from the lattice dynamics and the averaging over them has been already performed resulting in the correlation function of Eq. (8). Therefore, the infinite Liouville basis \(\left\{ \left\{ O_j \right\} \right\}\) appropriate for the present case does not need to contain components associated with the translational motion, it is sufficient to use the inner-sphere basis formed as a direct product of ortho-normal basis operators: \(\left\{ ABC \right\}\) for the distortional motion modeled as pseudorotational diffusion,\(^5,11,22,24\) \(\left\{ \text{LKM} \right\}\) for the molecular tumbling, and \(\left\{ \Sigma\sigma \right\}\) for the electron spin system: \(\left\{ \left\{ O_j \right\} \right\} = \left\{ \left\{ ABC \right\} \right\} \otimes \left\{ \text{LKM} \right\} \otimes \left\{ \Sigma\sigma \right\}\).\(^7,11,12\) This reduces very considerably the effective dimension of the matrix representation of the operator:

\[
\tilde{M}^{\text{Diff}}(u, \omega) = i\tilde{L}_{\text{L-Diff}}^{\text{Diff}} + \frac{D_{\text{Diff}}}{d^2} u^2 \tilde{I}^2 + i\omega_1 \tilde{I}^1
\]

and makes the calculations practicable. It might be useful to remind that the electron spin basis operators \(\left\{ \Sigma\sigma \right\}\) are related to the basis vectors \(\left\{ S, m \right\} \right\}\) forming the Liouville space for the \(S\) spin as follows:\(^11,12\)

\[
\left\{ \Sigma\sigma \right\} = \sum_m (-1)^{S-m-\sigma} \sqrt{2S+1} \left( S, m \right) \otimes \left( S, m + \sigma \right),
\]

where the \(\Sigma\) ranges from 1 to 2S. The distortional and rotational basis operators \(\left\{ ABC \right\}\) and \(\left\{ \text{LKM} \right\}\) are defined as

\[
\left\{ ABC \right\} = \left\{ ABC \right\} \left\{ \text{ABC} \right\} = \sqrt{24 + 1} \frac{D_{\text{Diff}}}{8\pi^2} \left\{ \text{ABC} \right\},
\]

The Wigner rotation matrices \(D_{\text{Diff}}^{\text{ABC}}(\left\{ \Omega_{P,P} \right\})\) and \(D_{\text{Diff}}^{\text{LKM}}(\left\{ \Omega_{P,L} \right\})\) are associated with the angles \(\Omega_{P,P}\) and \(\Omega_{P,L}\) describing the orientation of the principal axis system of the transient ZFS tensor with respect to the principal axis system of the static ZFS, and the orientation of the latter relative to the laboratory axes, respectively. Due to the appropriate normalization, the operators \(\left\{ O_j \right\}\) fulfill the condition: \(\left\{ O_j \right\} \left\{ O_j \right\} = \delta_{ij}\). The matrix elements of the Liouvilleans contributing to the operator \(M_{\text{Diff}}^{\text{Diff}}(u, \omega) = i\tilde{L}_{\text{L-Diff}}^{\text{Diff}} + \tilde{I}^2 + i\omega_1 \tilde{I}^1 + 1\), were, with exception of the term \((D_{\text{Diff}}/d^2)u^2\), evaluated in the context of the inner-sphere calculations and collected in Refs. 11 and 12. Thus, to set up the matrix representation of the \(M_{\text{Diff}}^{\text{Diff}}(u, \omega)\) operator, we need to evaluate only the remaining matrix elements corresponding to the operator \((D_{\text{Diff}}/d^2)u^2\). The evaluations are simple and one gets immediately:

\[
\left( A'B'C' \left\{ L' K' M' \right\} \left| \Sigma\sigma \right\{ D_{\text{Diff}}^{\text{Diff}}/d^2 \right| \left\{ \Sigma\sigma \right\} \left\{ \text{LKM} \right\} \right| ABC) = \delta_{A'A} \delta_{B'B} \delta_{C'C} \delta_{L'1} \delta_{K'1} \delta_{M'M} \delta_{\sigma \sigma} \left( \frac{D_{\text{Diff}}}{d^2} \right)^2.
\]

Then, the spectral density \(\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega)\) of Eq. (12) can be rewritten and further evaluated as a matrix product:

\[
\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega) = \sum_{p,q=1}^{1} \left( \begin{array}{ccc} 2 & 1 & 1 \\ 0 & p & -1 \\ 1 & q & -1 \end{array} \right) \int_0^\infty \text{Tr}(\tilde{K}^{\text{Diff}}(u, -\omega)) d\tau,
\]

One can identify, from Eq. (19), the role of the vector \(c_{1, \text{Diff}}\) [the index (Diff) refers to the translational diffusion]. This vector contains three nonzero elements associated with the basis vectors: \(\left\{ ABC \right\}\) \(\left\{ \text{LKM} \right\}\) \(\left\{ \Sigma\sigma \right\}\) of the Liouville space. The difference concerns the rotational states \(\left\{ \text{LKM} \right\}\). The fact that the rotational motion does not modulate directly the dipole-dipole interaction implies that the nonzero projection coefficients are now linked to the vectors corresponding to the rotational state \(\left\{ \text{LKM} \right\}\) = \(\left\{ 000 \right\}\) (since \(D_{\text{Diff}}^{\text{LKM}}(0,0,0) = D_{\text{Diff}}^{\text{LKM}}(0,1,1) = 1\)). According to Eq. (13), to obtain the nuclear spin relaxation rate \(K_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega)\) one has to integrate the \(\tilde{K}_{1,1,\text{Diff}}^{\text{DD}}(u, -\omega)\) spectral density over \(u\). This implies that one has to evaluate
The described procedure provides a very general recipe for the calculation of the dipolar spin relaxation in the presence of translational motion. It is a counterpart of the inner-sphere slow motion theory. Computational details are given in Sec. IV. Employing the general treatment of the nuclear spin relaxation modulated by translational motion, one can discuss the efficiency of the resulting nuclear spin relaxation for arbitrary conditions. Section V is devoted to this subject.

IV. COMPUTATIONAL DETAILS

The computational complexity of the outer-sphere PRE compared to the inner-sphere PRE results from the integration over the \( u \) variable, according to Eq. (13). The spectral density \( \tilde{K}^{DD,\text{Diff}}_{1,1}(u, -\omega) \) for a given \( u \) value is calculated in analogy to the inner-sphere case.\(^{12}\) The procedure for inverting the supermatrix \( \tilde{M}^{\text{Diff}}(u, \omega) \) [Eq. (14)] is based on the Lanczos algorithm.\(^{46}\) The spectral density \( \tilde{K}^{DD,\text{Diff}}_{1,1}(u, -\omega) \) is determined by a \( 3 \times 3 \) block of the inverted matrix. Since the translational degrees of freedom can be separated from the remainder of the lattice dynamics, they do not need to be included into the Liouville basis \( \{ O_j \} \). Therefore, the dimension of the supermatrix \( \tilde{M}^{\text{Diff}}(u, \omega) \) corresponds to the dimension of the inner-sphere supermatrix. As mentioned by Belorizky et al.,\(^{6} \) for the largest \( A \) and \( L \) values (for distortion and rotation, respectively) set to eight, the time needed for a single point calculation does not exceed a minute (on a single-processor computer) for most cases. Nevertheless, the calculations of the outer-sphere PRE (of the spectral density \( K^{DD,\text{Diff}}_{1,1}(-\omega) \)) require performing the integration of \( K^{DD,\text{Diff}}_{1,1}(u, -\omega) \) according to Eq. (13). In consequence, the time of a single point outer-sphere PRE calculation becomes longer by a factor equal to the number of steps over \( u \) needed for the integration. The integration limits, as well as the number of integration steps, depend on the translational diffusion coefficient \( D_{\text{Diff}} \). However, from the perspective of a user, it would be highly inconvenient to modify these parameters depending on the particular \( D_{\text{Diff}} \) value. Therefore, one should find a compromise between the accuracy of the integration (for a broad range of the translational diffusion coefficients) and the number of integration steps (i.e., the computatal time), taking also into account that the appropriate integration limits depend on \( D_{\text{Diff}} \). For the range of diffusion coefficients used in this paper \( [D_{\text{Diff}}=(2.0 \times 10^{-10}) - (2.3 \times 10^{-9}) \text{m}^2/\text{s}] \), the parameters: \( u_{\text{min}}=0.05, \ u_{\text{max}}=10.0, \) and \( N_{\text{int}}=100 \) \( (N_{\text{int}} \) is the number of integration steps between \( u_{\text{min}} \) and \( u_{\text{max}} \)) are appropriate. For a considerably slower or faster translational diffusion, the parameters should be suitably altered to improve the accuracy of the integration. Since one can hardly decrease \( N_{\text{int}} \), the required computational time becomes very long: to calculate an outer-sphere relaxation profile consisting of ten points (that is a minimum) one needs \( 15-20 \) h. Such a long computational time is not convenient for practical purposes. This problem could be solved by parallelizing the program, which we have not attempted at this stage. Alternatively, the computational time can be shortened by reducing the maximum values of the distortional and (or) rotational quantum numbers. The calculations presented in this paper have been done for the largest \( A \) and \( L \) values set to four. The program (with \( A=L=4 \)) has been tested against the low field analytical relaxation formulas provided in Ref. 21 for a broad range of diffusion coefficients and different electron spin quantum numbers. It has been found that, except for the case of a rather large static ZFS \( (\Delta_S \geq 0.5 \text{ cm}^{-1}) \) in combination with a high spin quantum number, the discrepancies do not exceed 10%. Setting \( A=L=4 \) (rather than 8), one can reduce the computational time by a factor of about 4; we consider this as an acceptable compromise. However, for a large static ZFS and high spin quantum numbers one should increase the maximum distortional and (or) rotational quantum numbers to eight.

All calculations in this work are performed assuming cylindrically symmetric static and transient ZFS tensors, \( \tau_{z}=E_{z}=0 \). It has been shown before that the rhombicity of the ZFS tensor is important for the PRE at low field, in particular for the integer spin quantum number,\(^{11,12,40,47} \) but we judge that the rhombic case is outside of scope of this work. For the axially symmetric ZFS, it is common to characterize the ZFS interaction strengths by parameters \( \Delta_S = \sqrt{2/3} \Delta_S \) and \( \Delta_T = \sqrt{2/3} \Delta_T. \) In addition, we assume that the principal frames of the intramolecular dipole-dipole interaction (the \( M \)-frame) and the static ZFS interaction (the \( P_T \) frame) coincide.

The following comparisons give an illustration of the computational accuracy of the present software: for \( S=1, \ \Delta_T=\Delta_S=0, \ \tau_{z}=0.5 \mu s, \ d=300 \text{ pm}, \ D_{\text{Diff}}=2.3 \times 10^{-9} \text{m}^2/\text{s}, \) the low field limit analytical formulas of Ref. 21 yield \( R_{1}^\text{outer}=1.08 \ (\text{mM s}^{-1}) \), while the present calculations give: \( R_{1}^\text{outer}=1.17 \ (\text{mM s}^{-1}) \) for both \( A=L=8 \) and \( A=L=4. \) For a large static ZFS, \( D_{\text{z}}=(3/2)\Delta_S=10^{-1 \text{ cm}^{-1}} \ (\Delta_T=0, \ \tau_{z}=1 \mu s, \ d=300 \text{ pm}, \ D_{\text{Diff}}=2.3 \times 10^{-9} \text{m}^2/\text{s}) \), the analytical low field limit\(^{21} \) gives \( R_{1}^\text{outer}=0.36 \ (\text{mM s}^{-1}) \), while from the present calculations one obtains \( R_{1}^\text{outer}=0.385 \ (\text{mM s}^{-1}) \) for \( A=L=8 \) and 0.39 (\text{mM s}^{-1}) for \( A=L=4. \) The description of the outer-sphere relaxation for slowly rotating systems under the assumption that the electron spin is within the Redfield limit\(^{25} \) serves as another source of comparison. For example, for \( S=1, \ D_{\text{z}}=0.02 \text{ cm}^{-1}, \ D_{\text{y}}=0.05 \text{ cm}^{-1}, \ \tau_{z}=1 \mu s, \ d=300 \text{ pm}, \ D_{\text{Diff}}=2.3 \times 10^{-9} \text{m}^2/\text{s}, \) the treatment of Ref. 22 predicts (at low field) \( R_{1}^\text{outer}=0.84 \ (\text{mM s}^{-1}) \), while the present treatment gives \( R_{1}^\text{outer}=0.91 \ (\text{mM s}^{-1}) \); at high field (10 T) the results are \( R_{1}^\text{outer}=0.297 \ (\text{mM s}^{-1}) \) and \( R_{1}^\text{outer}=0.295 \ (\text{mM s}^{-1}) \) for the treatment of Ref. 22 and the present one, respectively. For a slower translational diffusion, \( D_{\text{Diff}}=0.5 \times 10^{-9} \text{m}^2/\text{s} \) (and other parameters remain-
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ing  unchanged), one gets \( R_{\text{outer}} = 2.85 \text{ (mM s)}^{-1} \) and \( R_{\text{inner}} = 3.06 \text{ (mM s)}^{-1} \) at low field from the approach of Ref. 22 and using the present software, respectively. At high field (10T), the corresponding values are \( R_{\text{outer}} = 1.06 \text{ (mM s)}^{-1} \) (Ref. 22) and \( R_{\text{outer}} = 1.045 \text{ (mM s)}^{-1} \) (present method).

V. EXAMPLES OF OUTER-SPHERE PRE AND DISCUSSION

The relaxivity (spin-lattice relaxation enhancement at 1 mM paramagnetic species) is given as a sum of the inner- and outer-sphere contributions:

\[
\text{PRE} = R_{1p}q + R_{1\text{ outer}} = R_{1\text{ inner}} + R_{1\text{ outer}}.
\]

Here, \( R_{1p} \) is the inner-sphere paramagnetic relaxation enhancement \([R_{1p}=2K_{1}(\omega_I)]\), \( p \) is the ratio of the molar concentrations of paramagnetic species (1 mM) and the free ligand/solvent. In the following, we assume that the ligand/solvent is water. Then, \( q \) is the number of water molecules in the coordination shell. The free water concentration in pure water is 55.6 M. Thus, for proton relaxation in 1 mM solution of a paramagnetic species in water, we get \( R_{1\text{ inner}} = qR_{1p} = 55.6 \times 10^3 \). We should not forget that the outer-sphere term is explicitly concentration dependent, through the \( N_S \) factor in Eq. (13). At 1 mM concentration of paramagnetic species, the \( N_S \) (in units of \( \text{m}^{-3} \)) takes on the value of the Avogadro number \((6.022 \times 10^{23})\). In Eq. (21), the exchange lifetime between the coordination shell and the bulk solvent has been neglected. The calculations presented in this section have been performed assuming very fast exchange process and setting \( q=1 \). The inner-sphere relaxation profiles have been calculated for the interspin distance \( r_{IS} = 300 \text{ pm} \), while the distance of closest approach for the outer sphere has been set to \( d = 380 \text{ pm} \). The distortional correlation time used in all calculations is \( \tau_T = 5 \text{ ps} \).

We begin the discussion of the outer-sphere relaxivity with the case of \( S=\frac{7}{2} \), which applies for Gd (III) complexes. Figures 2–4 correspond to three combinations of the transient and static ZFS parameters: \( \Delta_T = 0.01 \text{ cm}^{-1}, \Delta_S = 0.01 \text{ cm}^{-1}, \Delta_T = 0.01 \text{ cm}^{-1}, \Delta_S = 0.05 \text{ cm}^{-1} \) and \( \Delta_T = 0.05 \text{ cm}^{-1}, \Delta_S = 0.01 \text{ cm}^{-1} \), respectively. For every combination of \( \Delta_T \) and \( \Delta_S \), we have done the calculations for four translational diffusion coefficients: \( D_{\text{Diff}} = 2.3 \times 10^{-9} \text{ m}^2/\text{s} \) (water diffusion coefficient at room temperature), \( D_{\text{Diff}} = 1.15 \times 10^{-9} \text{ m}^2/\text{s} \), \( 0.5 \times 10^{-9} \text{ m}^2/\text{s} \), and \( 0.2 \times 10^{-9} \text{ m}^2/\text{s} \). For the first three diffusion coefficients (in combination with various \( \Delta_T \) and \( \Delta_S \)), the calculations have been carried out for four rotational correlation times, including a case of slow molecular tumbling: \( \tau_R = 100 \text{ ps}, 500 \text{ ps}, 1 \text{ ns}, \text{ and } 1 \mu s \) (slow rotation). The rotational correlation time and the mutual diffusion coefficient are both related to the solvent viscosity (Stokes–Einstein–Debye and Stokes relations). Therefore, for the slowest translational diffusion \( (D_{\text{Diff}} = 0.2 \times 10^{-9} \text{ m}^2/\text{s}) \), we have excluded the shortest correlation time, \( \tau_R = 100 \text{ ps} \). In this way, we have covered a broad range of parameters relevant for the outer-sphere contribution to the spin-lattice relaxivity.

\[ \text{FIG. 2. (A) Ratio between outer-sphere and inner-sphere relaxivities at low field versus the translational diffusion coefficient for the spin quantum number } S=\frac{7}{2}. \quad \Delta_T=0.01 \text{ cm}^{-1}, \Delta_S=0.01 \text{ cm}^{-1}, \text{ and } \tau_R=5 \text{ ps }, \tau_E=300 \text{ ps}, d = 380 \text{ pm}. \text{ Inner-sphere relaxation has been calculated assuming that exchange of solvent molecules is fast and the number of water molecules in the coordination sphere is } q=1. \text{ The inset shows the corresponding values of the outer-sphere relaxation at low field limit. (B) Outer-sphere relaxation profiles corresponding to selected cases presented in (A). Solid lines: } \tau_E = 100 \text{ ps, dashed-dotted line: } \tau_E=500 \text{ ps, dashed line: } \tau_E=1 \text{ ns, dotted lines: } \tau_E=1 \text{ \mu s.} \]

Figure 2(A) shows the ratio between the outer- and inner-sphere relaxivities at low field (1.0 \( \times 10^{-4} \) T) for \( \Delta_T = 0.01 \text{ cm}^{-1}, \Delta_S=0.01 \text{ cm}^{-1} \) plotted versus the translational diffusion coefficient for different rotational correlation times, while the inset shows the values of \( R_1 \text{ outer/} R_1 \text{ inner} \) increases when the molecular tumbling becomes faster, i.e., the contribution of the outer-sphere relaxivity becomes more significant. In the case of inner-sphere relaxation, the molecular tumbling plays a double role: it directly modulates the I-S dipole-dipole interaction and affects the electron spin dynamics (and in consequence the nuclear spin relaxation) as a source of modulations of the ZFS interaction. The rotational motion modulates the orientation of the principal axis system of the static ZFS \( (P_S) \) and contributes to the modulations of the orientation of the \( (P_I) \).
frame; however, the distortional motion is usually the main source of modulations in the latter case. In the case of outer sphere, the dipole-dipole interaction fluctuates due to the translational diffusion and the molecular tumbling affects the nuclear spin relaxation only via the ZFS interaction. In consequence, the inner-sphere relaxation is more sensitive to the rotational correlation time, faster molecular tumbling decreases its value more significantly than is the case for the outer-sphere relaxation. In the outer-sphere case, there are two sources of fluctuations of the dipole-dipole interaction: the translational diffusion and the electron spin dynamics (relaxation). If the translational diffusion dominates (i.e., if it is fast), the molecular tumbling has no significant influence on the outer-sphere relaxation. This can be seen in the inset of Fig. 2(A). Figure 2(B) shows outer-sphere relaxation profiles corresponding to selected cases presented in Fig. 2(A). For slower translational diffusion, the effect of molecular tumbling on the outer-sphere relaxation is more pronounced. Moreover, we can also notice in the inset of Fig. 2(A) and in Fig. 2(B) that, for the slow diffusion case, the outer-sphere relaxivity at low field increases with increasing $\tau_R$, which can be related to the slowing down the electron spin relaxation outside of the Redfield limit. These effects can be observed over a wide range of magnetic fields, cf. Figure 2(B) where we can see relaxation profiles for different rotational correlation times and diffusion coefficients. In general, the outer-sphere relaxation rate increases for slower translational diffusion. Thus, its contribution to the total relaxivity becomes larger for slower translational diffusion and faster reorientation. We note, however, that the electron spin relaxation becomes slower for high magnetic fields. Thus, the translational diffusion becomes under these conditions the dominant contribution to the modulations of the dipole-dipole interaction and the outer-sphere relaxivity is practically independent of the rotational correlation time.
TABLE I. Calculated low field (10^{-4} T) values of outer-sphere relaxivity for different translational diffusion coefficients, including and excluding static ZFS. All calculations use \( S=7/2 \), \( \tau_R = 1 \ \mu s \), \( \tau_T = 5 \ \text{ps} \), and the same geometric parameters as in Figs. 2–4.

<table>
<thead>
<tr>
<th>( D_{\text{diff}} ) (m^{2} s^{-1})</th>
<th>( R_1 ) outer (mM s^{-1}) ( \Delta_S=0.01 ) cm^{-1}</th>
<th>( R_1 ) inner (mM s^{-1}) ( \Delta_S=0.01 ) cm^{-1}</th>
<th>( R_1 ) outer (mM s^{-1}) ( \Delta_S=0 ) cm^{-1}</th>
<th>( R_1 ) inner (mM s^{-1}) ( \Delta_S=0 ) cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 \times 10^{-9}</td>
<td>5.7</td>
<td>6.7</td>
<td>4.6</td>
<td>4.9</td>
</tr>
<tr>
<td>1.15 \times 10^{-9}</td>
<td>10.3</td>
<td>13.0</td>
<td>7.5</td>
<td>8.3</td>
</tr>
<tr>
<td>0.5 \times 10^{-9}</td>
<td>20.0</td>
<td>27.9</td>
<td>12.4</td>
<td>14.4</td>
</tr>
<tr>
<td>0.2 \times 10^{-9}</td>
<td>40.1</td>
<td>62.7</td>
<td>18.7</td>
<td>23.3</td>
</tr>
</tbody>
</table>

It is interesting to compare the low field values of the outer-sphere relaxivity as shown in Fig. 2(A) with corresponding values obtained for the static ZFS set to zero. We can use the latter values as corresponding to the Zeeman limit or SBM-like theories (yet retaining in principle the multiexponential nature of electron spin relaxation). Essentially, SBM-like theories (neglecting the static ZFS interaction) do not predict a dependence of the outer-sphere relaxivity on the rotational correlation time. The \( R_1 \) outer values for \( \Delta_S=0 \), \( \tau_T = 1 \ \mu s \) and different translational diffusion coefficients are compared to the corresponding values of Fig. 2(A) (\( \Delta_S=0.01 \) cm^{-1}) in Table I. This comparison clearly shows that the discrepancies at the low field limit between the present treatment and the SBM-like approach are significant. The differences at higher field are expected to be smaller.\(^{37,30}\)

Figure 3 shows the effects of the increased static ZFS on the outer-sphere relaxivity and the \( R_1 \) outer/\( R_1 \) inner ratio. From the inset in Fig. 3(A), one can again see that, for fast translational diffusion, the electron spin dynamics is masked by the translational motion and the static ZFS does not influence much the outer-sphere relaxation. For slow molecular tumbling, the static ZFS affects the energy level structure of the electron spin and influences in this way the nuclear spin relaxation. Fast translational diffusion leads also in this case to a kind of “extreme narrowing” and the ZFS contribution to the electron spin energy level structures becomes less relevant. For slower translational motion, the outer-sphere relaxation becomes more sensitive to the static ZFS. Comparing Figs. 2(A) and 3(A), one can conclude that the ratio \( R_1 \) outer/\( R_1 \) inner changes due to effects of the static ZFS on both the outer- and the inner-sphere relaxation (in this case, the inner-sphere contribution becomes more sensitive to the static ZFS for slow rotation). Actually, for slow rotation, the \( R_1 \) outer/\( R_1 \) inner factor is smaller for a larger static ZFS. On the other hand, a larger static ZFS leads to a more pronounced dependence of the outer-sphere relaxation on the molecular tumbling. This can be seen comparing Figs. 2(B) and 3(B). Differences between results of the present theory and the SBM-like approach are in this case even larger than for the low static ZFS.

A larger transient ZFS causes a faster electron spin relaxation and, in consequence, reduces the effects of the static ZFS (depending on the time scale of the rotational motion, we can talk about reducing the relative contribution of the static ZFS to the electron spin relaxation or about masking the ZFS effect on the electron spin energy level structure).

One can see this in Fig. 4, presenting the numerical results for a rather large transient ZFS (\( \Delta_T=0.05 \) cm^{-1}) and a small static ZFS (\( \Delta_S=0.01 \) cm^{-1}). In this case, the outer-sphere relaxation does not depend significantly of the molecular tumbling. However, since the rotational motion directly modulates the dipole-dipole coupling in the inner-sphere case, the ratio \( R_1 \) outer/\( R_1 \) inner depends on the rotational correlation time. Even though the large transient ZFS reduces the values of the outer-sphere PRE compared to the case of Fig. 2(A), the \( R_1 \) outer/\( R_1 \) inner factors are larger compared to Fig. 2(A), except of the case of fast reorientational motion. It is so because the large transient ZFS reduces the inner-sphere relaxivity to a larger extent than its outer-sphere counterpart. This effect does not concern the case of fast molecular tumbling, since the rotational contribution to the modulations of the dipole-dipole interaction overruns in this limit the electron spin relaxation. Examples of outer-sphere relaxation profiles, corresponding to Fig. 4(A), are presented in Fig. 4(B). Again, we estimate the SBM-like outer-sphere relaxivities by setting \( \Delta_S=0 \). Also these results are shown in Table I. Since in this case the electron spin dynamics is faster it masks to a certain extent the effect of the static ZFS interaction, but it is still relevant.

Outer- and inner-sphere relaxation profiles have different shapes and, therefore, the \( R_1 \) outer/\( R_1 \) inner ratio changes with the magnetic field. Thus, the outer-sphere contributions modify overall shapes of NMRD profiles. Examples of field dependencies of the \( R_1 \) outer/\( R_1 \) inner ratio for the spin quantum number \( S=7/2 \) are presented in Fig. 5.

Next, we turn attention to the case of \( S=1 \), which for example corresponds to Ni (II) complexes. Nickel (II) complexes are, in general, characterized by much bigger ZFS values, because of less symmetric electronic structure. Figure 6(A) shows the \( R_1 \) outer/\( R_1 \) inner ratio and the \( R_1 \) outer values at low magnetic field. The transient ZFS has been set to \( \Delta_T=1 \) cm^{-1}, which implies a fast electron spin relaxation. Since the static ZFS is at the same time even larger (\( \Delta_S=5 \) cm^{-1}), it might also contribute significantly to the electron spin relaxation. This effect is seen in the inset of Fig. 6(A), in particular, for the rotational correlation time \( \tau_T = 100 \) ps and slower translational diffusion. Since the direct rotational modulation of the dipole-dipole interaction for the inner-sphere case is now masked by the electron spin relaxation, the \( R_1 \) outer/\( R_1 \) inner ratio is practically independent of the rotational correlation time. In Fig. 6(B), we present examples of the outer-sphere relaxation profiles corresponding to Fig.
6(A). At low magnetic field, the electron spin relaxation is faster and, therefore, the ratio does not depend very significantly on the translational diffusion coefficient, while for high fields this dependence is much more pronounced. In this case, the perturbation approach to the electron spin relaxation fails badly; the predictions of the SBM-like description ($\Delta_S=0$) are physically reasonable and yield the following results at the low field limit ($\Delta_T=1$ cm$^{-1}$, $T_R=1$ $\mu$s): $D_{\text{Diff}}=2.3 \times 10^{-9}$ m$^2$/s; $R_1$ outer =0.18 (1/mM s); $D_{\text{Diff}}=1.15 \times 10^{-9}$ m$^2$/s; $R_1$ outer =0.21 (1/mM s); $D_{\text{Diff}}=0.5 \times 10^{-9}$ m$^2$/s; $R_1$ outer =0.24 (1/mM s); and $D_{\text{Diff}}=0.2 \times 10^{-9}$ m$^2$/s; $R_1$ outer =0.25 (1/mM s). Here, the discrepancies between the complete description including the static ZFS interaction and the SBM-like description are even larger than for the $S=\frac{1}{2}$ case.

Figure 7 displays the $R_1$ outer/$R_1$ inner ratio as a function of the magnetic field for $S=1$, in analogy to Fig. 5. At low magnetic field, the electron spin relaxation dominates over the rotational contribution to the modulations of the dipole-dipole axis for the inner-sphere case; for that reason, the ratio is independent of the rotational correlation time. Since electron spin relaxation slows down for higher magnetic fields, the rotational motion influences the $R_1$ outer/$R_1$ inner ratio in that range.

In a recent study, we investigated proton NMRD profiles for the nickel (II) ion solutions in water and water-glycerol mixtures. Fitting the calculated data to the experiments was carried out including only the inner-sphere contributions; the outer-sphere parts were estimated a posteriori for the cases with highest and lowest viscosity, based on the parameters obtained from the fitting and on the theory of the present paper. Unfortunately, the estimates presented in that study were erroneous. The correct values for the $R_1$ outer/$R_1$ inner ratio in the low-viscosity case (no glycerol, 343 K) are 0.12–0.16 ($d=350$ pm, $D_{\text{Diff}}=5.6 \times 10^{-9}$ m$^2$/s) depending on the field, while for the high viscosity case (glycerol55%, 323 K) the corresponding numbers are 0.10–0.23 (parameters of line 4, Table III in Ref. 51, and $d=350$ pm, estimated $D_{\text{Diff}}=0.7 \times 10^{-9}$ m$^2$/s). For the case of 1 mM Ni(II) in the (acidified) water, the $pq$ value to be used in Eq. (21) is $6 \times 1/(55.6 \times 10^{3})=1.08 \times 10^{-4}$, while the corresponding number for 1 mM Ni(II) in glycerol55% solution is $1.39 \times 10^{-4}$. The $N_3$ value, relevant for $R_1$ outer, is in both cases $6.022 \times 10^{23}$ m$^{-3}$.

VI. CONCLUDING REMARKS

The theory for outer-sphere paramagnetic relaxation enhancement, derived in this paper, is a counterpart of the general treatment of inner-sphere paramagnetic relaxation enhancement. Since it is also based on expressing the lattice Liouvillian as a supermatrix in a vector space defined by a suitable set of lattice parameters, it can be applied beyond...
validity regimes of perturbation approaches. The main theoretical and computational complexity is due to the nonexponential form of the correlation function for translational motion, which requires numerical integration leading to a very considerable increase in the computational time. The theory is used to discuss the contribution of the outer-sphere relaxation to the total relaxivity at low magnetic field, and as a function of the magnetic field strength. The relative magnitudes of the inner- and outer-sphere relaxivities are calculated for different values of the translational diffusion coefficient, the rotational correlation time, and the parameters responsible for the electron spin dynamics, i.e., the ZFS interaction and the distortional correlation time. The calculated examples lead to the general conclusion that, for most cases, the outer-sphere contribution is relevant and should be included into the analysis of NMRD relaxation profiles. This conclusion is reached assuming the force-free translational diffusion and for a specific set of dipolar interaction strength parameters, the electron spin—nuclear spin distance for the inner-sphere and the distance of closest approach for the outer-sphere case. The inner-sphere contribution scales as $r_0^{-6}$, the outer-sphere part approximately as $d^{-3}$ [this scaling has been derived under simplifying conditions by Abragam; here, the situation is more complicated because $d$ appears under the integral sign in Eqs. (10)–(12)]. Thus, the relative importance of the outer-sphere mechanism would decrease if the distance of closest approach was assumed larger with respect to the inner-sphere interspin distance. Independently of the interaction strengths, we note that the outer-sphere contribution is most relevant for slow translational diffusion and fast molecular tumbling, while the role of the outer-sphere relaxation is less important for slowly rotating systems and fast translational diffusion.

ACKNOWLEDGMENTS

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