

ESR SPECTRA FOR HIGH-SPIN SYSTEMS UNDER ARBITRARY MOTION CONDITIONS

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A general theory of Electron Spin Resonance (ESR) lineshape analysis is presented. The theory concerns high-spin systems, for which the dominating contribution to the electron spin dynamics is provided by zero-field splitting. The approach is based on a full solution of the stochastic Liouville - von Neumann equation, and, in consequence, it is valid for arbitrary motional conditions and interaction strengths.

INTRODUCTION

Perturbation approaches give a valuable insight into electron spin relaxation, but many systems violate the assumptions of the perturbation theory (Slichter, 1990; Kruk, 2007). Very often amplitudes of the zero field splitting and the Zeeman interaction combined with motional conditions bring the electron spin beyond the validity regimes of Redfield relaxation theory (Slichter, 1990) requiring that the amplitude of the interaction causing relaxation multiplied by the characteristic correlation time gives a value much smaller than one, and then the spin relaxation times cannot be explicitly defined. This fact has led to developing general (slow motion) treatments based on the stochastic Liouville equation (SLE). The name "slow motion" originates from the situation when the mean interaction strength is larger than, or comparable to, the inverse of the correlation time that corresponds to the motion modulating the interaction. The methods based on the stochastic Liouville equation were introduced by Freed and co-workers (Freed, 1976; Schneider & Freed, 1989) to describe ESR lineshapes for systems with the electron spin quantum number $S = 1/2$, including interactions with neighbouring nuclear spins under very general anisotropic motional conditions. In this work we propose an extension of this treatment to an arbitrary electron spin quantum number.

SPIN HAMILTONIAN

The total electron spin Hamiltonian, $H(S)$ can be decomposed into a sum of three main terms in the following way:

$$H(S) = H_Z + H_{HC} + H_{ZFS} \quad (1)$$

The first term, H_Z , describes the Zeeman interaction and includes the g-tensor (or g-factor if the tensor is isotropic). In the last case this term has the simple form, $H_Z = \omega_S S_z$, where ω_S is the electron frequency. The second term, H_{HC} , describes the hyperfine coupling between the electron spin and the metal nucleus. The g-anisotropy and the hyperfine coupling are most important for $S = 1/2$; they are the predominant mechanisms for the spin relaxation. These mechanisms may be of importance for high-spin systems if the ground state is an S state, which is the case for Mn^{2+} ($S = 5/2$). The third term, H_{ZFS} , describes the zero-field splitting (ZFS), which is present for electron spin systems of $S > 1/2$ and in most cases dominates the spin dynamics. The origin of the ZFS interaction for transition metal complexes is due to the second-order effects of the spin-orbit coupling. However, for other systems such as radicals, a direct dipole-dipole interaction between the unpaired electrons leads to the ZFS (Griffith, 1961). The formal expression of the ZFS Hamiltonian is the same irrespective of the physical origin. In the principal axis system of the ZFS tensor (P) it takes the form:

$$H_{ZFS}^{(P)} = \sqrt{\frac{2}{3}} D T_0^2(S) + E(T_{-2}^2(S) + T_2^2(S)) \quad (2)$$

where the quantities D and E describe the axial and rhombic components of the static (permanent) ZFS tensor, respectively (here we limit ourselves to the second order terms). The tensor operators are defined as:

$$T_0^2(S) = \frac{1}{\sqrt{6}} [3S_z^2 - S(S+1)], \quad T_{\pm 1}^2(S) = \mp \frac{1}{2} [S_z S_{\pm} + S_{\pm} S_z]$$

and $T_{\pm 2}^2(S) = \frac{1}{2} S_{\pm} S_{\pm}$. For a detailed treatment of the ZFS the reader is referred to (Rudowicz & Misra, 2001). The explicit form of $H_{ZFS}^{(P)}$ depends on the symmetry of the complex given by a point symmetry group (Rudowicz & Gnutek, 2009). The symmetry of the ligand field also plays an important role for the degeneracy of the electron spin energy levels. For example, complexes of $S = 1$ and $S = 3/2$ with cubic symmetry have no static component of the ZFS, hence the S manifold is not split. A fluctuating ZFS is, however, always present for $S \geq 1$, which temporarily lifts the degeneracy. Physically, the fluctuating (transient) ZFS is due to deformations in the ligand framework, which is caused by collisions of solvent molecules, by damped vibrations in the complex, and by any other local motion that causes the ZFS to fluctuate in time. The total ZFS Hamiltonian, can then be decomposed into the static, H_{ZFS}^S , and transient, H_{ZFS}^T , parts:

$$H_{ZFS} = H_{ZFS}^S + H_{ZFS}^T \quad (3)$$

The forms of the static and transient ZFS (in the laboratory frame, i.e. the frame determined by the external magnetic field) depend on the assumed models of motion (Kruk, 2007; Rudowicz & Misra, 2001; Rudowicz & Gnutek, 2009). Since the static zero field splitting is a part of the entire ZFS, obtained as a result of averaging over molecular distortions (vibrations), it is only mediated by the molecular tumbling (reorientational motion). This implies that the static ZFS becomes time dependent in the laboratory (L) frame:

$$H_{ZFS}^{S(L)}(t) = \sqrt{\frac{2}{3}} D_S \sum_{m=-2}^2 (-1)^m \left(\sum_{k=-2}^2 V_k^{2S(P_S)} D_{k,-m}^2(\Omega_{P_S L}(t)) \right) T_m^2(S) \quad (4)$$

$$= \sum_{m=-2}^2 (-1)^m \tilde{V}_{-m}^{2S(L)}(t) T_m^2(S)$$

where

$$V_0^{2S(P_S)} = 1, \quad V_{\pm 1}^{2S(P_S)} = 0, \quad V_{\pm 2}^{2S(P_S)} = \frac{4}{\sqrt{6}} \frac{E_S}{D_S},$$

while

$$\tilde{V}_{-m}^{2S(L)} = \sqrt{\frac{2}{3}} D_S D_{0,-m}^2(\Omega_{P_S L}(t)) + E_S [D_{-2,-m}^2(\Omega_{P_S L}(t)) + D_{2,-m}^2(\Omega_{P_S L}(t))].$$

Here (P_S) indicates the principal axis system of the static ZFS tensor, while D_S and E_S denote the axial and rhombic component of the static ZFS. The reorientational motion mediating this interaction is modeled as isotropic rotational diffusion. The relative orientation of the (P_S) and (L) frames is described by the angle $\Omega_{P_S L}(t)$, ($\Omega \equiv (\alpha, \beta, \gamma)$) which varies in time due to this isotropic molecular tumbling. The simplest possible model (and therefore often used) of the transient ZFS assumes that has a constant magnitude and a principal direction (a principal axis system (P_T)), which is not fixed in the molecule (Kruk, 2007; Nilsson & Kowalewski, 2000; Kowalewski, Kruk & Parigi, 2005). The (P_T) frame changes its orientation relative to the (P_S) frame according to rotational diffusion equation (Kruk, 2007; Rudowicz & Misra, 2001; Rudowicz & Gnutek, 2009). Therefore this model is referred to in the literature as the ‘pseudorotational model’. For the purpose of evaluating ESR spectra one has to consider the transient ZFS in the laboratory frame, performing a two step transformation, explained in Fig. 1 and Fig. 2.

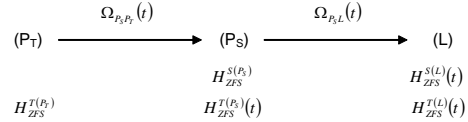


Fig. 1. Representation of the static and transient ZFS interactions depending on the reference frames.

The first transformation is between the (P_T) and (P_S) frames through the Euler angle $\Omega_{P_T P_S}(t)$ affected by the distortional motion, while the second transformation occurs between the (P_S) and laboratory (L) frames via the Euler angle $\Omega_{P_S L}(t)$ modulated by the molecular tumbling. The three relevant coordinate systems and the corresponding representations of the static and transient ZFS are presented in Fig. 2.

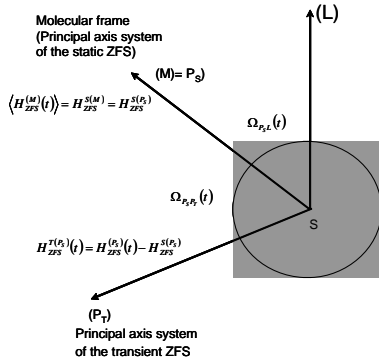


Fig. 2. A schematic view of the ZFS terms. The static ZFS interaction is defined as the averaged part of the entire ZFS interaction considered in a molecule fixed frame (M). For simplicity we have assumed that the molecular frame (a reference frame fixed in the molecule) coincides with the principal axis system of the static ZFS). The transient ZFS represents the momentary deviation of the ZFS interaction from its averaged value.

These two transformations lead to the following form of the transient ZFS Hamiltonian in the laboratory frame:

$$H_{ZFS}^{T(L)}(S)(t) = \sqrt{\frac{2}{3}} D_T \times \sum_{m=-2}^2 (-1)^m \left[\sum_{n=-2}^2 \left(\sum_{k=-2}^2 V_k^{2T(P)} D_{k,-n}^2(\Omega_{P,P}(t)) \right) D_{-n,-m}^2(\Omega_{P,L}(t)) \right] T_m^2(S) \quad (5)$$

$$= \sum_{m=-2}^2 (-1)^m \tilde{V}_{-m}^{2T(L)} T_m^2(S)$$

where

$$\tilde{V}_{-m}^{T(L)} = \sum_{n=-2}^2 \left\{ \sqrt{\frac{2}{3}} D_T D_{0,-n}^2(\Omega_{P,P}(t)) + E_T [D_{-2,-n}^2(\Omega_{P,P}(t)) + D_{2,-n}^2(\Omega_{P,P}(t))] \right\} D_{-n,-m}^2(\Omega_{P,L}(t))$$

Here D_T and E_T denote the axial and rhombic components of the fluctuating ZFS.

THEORETICAL BACKGROUND OF THE SPECTRAL ANALYSIS

An ESR lineshape function $L(\omega_S - \omega)$ is determined by the spectral density:

$$s_{-1,-1}(\omega) = \int_0^\infty \langle S_{-1}^+(\tau) S_{-1}(0) \rangle \exp(-i\omega\tau) d\tau \quad (6)$$

$(L(\omega_S - \omega) \propto s_{-1,-1}(\omega))$ corresponding to the single-quantum spin transitions (Kruk, 2007). More explicitly the lineshape function is given as (Kruk, 2007):

$$L(\omega_S - \omega) = \int_0^\infty Tr_S \left\{ S_{-1}^{1+} \left[\exp(-i\hat{L}_L \tau) S_{-1}^1 \right] \rho_S^{eq} \right\} \exp(-i\omega\tau) d\tau \quad (7)$$

$$\propto [S_{-1}^1]^\dagger \left[\hat{M}_{ESR} \right]^{-1} [S_{-1}^1]$$

The lattice Liouville operator, \hat{L}_L , contains all degrees of freedom that are relevant for the ESR spectrum: $\hat{L}_L = \hat{L}_Z(S) + \hat{L}_{ZFS}^S + \hat{L}_{ZFS}^T + \hat{L}_D + \hat{L}_R$. The contributing operators represent the Zeeman interaction for the spin S , the static and transient zero field splitting, distortional and rotational motions of the complex. According to the pseudorotational model (Kruk, 2007; Nilsson & Kowalewski, 2000; Kowalewski *et al.*, 2005) incorporated into the slow motion theory, the pseudorotational diffusion modulating the orientation of the principal axis system of the transient ZFS with respect to a molecule fixed frame is supposed to reflect any distortional motion of the molecule leading to stochastic fluctuations of the transient ZFS tensor.

The superoperator \hat{M}_{ESR} originating from the Liouvilian is defined as [3]:

$$\hat{M}_{ESR} = -i \left[\hat{L}_Z(S) + \hat{L}_{ZFS}^S + \hat{L}_{ZFS}^T + \hat{L}_R + \hat{L}_D + \hat{1}\omega \right] \quad (8)$$

The matrix form of the \hat{M}_{ESR} operator is set up in a basis $\{|O_i\rangle\}$ given as an outer product of vectors associated with the degrees of freedom of the system: $|O_i\rangle = |ABC\rangle \otimes |LKM\rangle \otimes |\Sigma\sigma\rangle$ [3,10,11] with the distortional, rotational and spin components $|ABC\rangle$, $|LKM\rangle$ and $|\Sigma\sigma\rangle$, respectively.

Some examples of ESR spectra calculated in this way are shown in Fig. 3.

After having explained the general approach we shall comment in more detail about the validity regimes of the perturbation approach.

LIMITATIONS OF THE PERTURBATION APPROACH

One can provide an analytical description of the ESR lineshape only if the spin system is within the Redfield limit (Slichter, 1990; Kruk, 2007). This means that the product of the amplitude of the static ZFS and the rotational correlation time, $\omega_{ZFS}^S \tau_R$, is crucial for the explicit, clear definition of the electron spin relaxation. ESR spectra are collected at rather high magnetic fields

compared to NMR experiments. The so called X band corresponds to the magnetic field of 0.3-0.35T, while the Q and W bands are measured at 1.1-1.3T and 3.3-3.5T, respectively. Therefore, if the condition $\omega_{ZFS}^S \tau_R \ll 1$ is fulfilled, the static ZFS provides, beside the transient ZFS (if $\omega_{ZFS}^T \tau_D \ll 1$) a relaxation channel for the electron spin. In this case the operator \hat{M}_{ESR} takes the form:

$$\hat{M}_{ESR} = -i\hat{L}_Z(\omega_s) + \hat{R}_{ZFS}^{S(S)}(\omega_s) + \hat{R}_{ZFS}^{S(T)}(\omega_s) - i\omega\hat{1} \quad (9)$$

In the opposite motional regime, when the molecular frame (the principal axis system of the static ZFS tensor) is fixed relative to the laboratory frame, the static ZFS modifies the energy level structure of the electron spin. One can argue that typically the amplitude of the static ZFS is rather small comparing to the amplitude of the Zeeman coupling for the magnetic field at which the ESR spectra are measured and therefore it can be neglected altogether. This way of thinking is quite dangerous. It is not enough to compare just the amplitudes of the ZFS and Zeeman couplings.

The vector $[S_{-1}^1]$ contains expansion coefficients of the tensor operator S_{-1}^1 in the basis $\{|O_i\rangle\}$. In fact, there is just one non-zero coefficient, namely the one associated with the basis vector $|ABC\rangle|LKM\rangle|\Sigma\sigma\rangle = |000\rangle|000\rangle|1-1\rangle$. Thus the ESR lineshape is determined by one element of the inverted matrix $[\hat{M}_{ESR}]^{-1}$. The parameters are typical for Gd^{3+} complexes used as contrast agents in NMR tomography.

To be sure that the effect of the static ZFS is negligible one has to take into account how these two interactions influence the electron spin energy levels. To illustrate this statement let us consider the case of $S = 7/2$. To simplify the problem, we assume that the molecular and the (P_s) frames coincide. The basis appropriate for the spin quantum number $S = 7/2$ consists of $(2S + 1) = 8$ functions formed by the Zeeman states $\{|m_s\rangle\}$ (m_s is the magnetic spin quantum number).

The matrix element of the static Hamiltonian H_0^S including the Zeeman coupling as well as the static ZFS, $H_0^S = H_Z(S) + H_{ZFS}^S$ taken between the states of $m_s = \frac{1}{2}$ is

$$\text{equal to: } \left\langle \frac{1}{2} \left| H_0^S \right| \frac{1}{2} \right\rangle = -5D_s + \frac{1}{2}\omega_s$$

One can see from this expression that the real effect of the static ZFS is by factor 10 higher than one could expect comparing only the strengths of the two terms. This example should be treated as a warning that a relatively weak interaction can alter significantly the

energy level structure and such effects have to be always treated with caution.

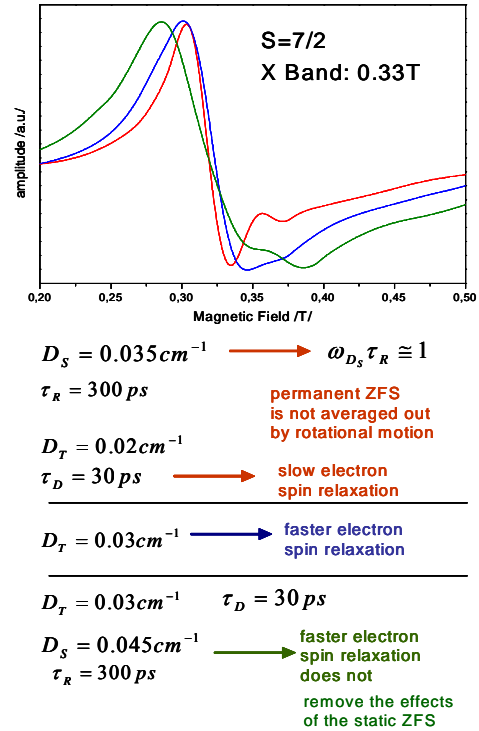


Fig. 3. Examples of ESR spectra, D_s, D_T - axial parts of the static and transient zero field splitting, respectively, τ_R - rotational correlation time, τ_D - distortional correlation time.

When the static ZFS tensor is fixed with respect to the laboratory frame, the operator \hat{M}_{ESR} must be defined for every molecular orientation. It includes then the main Liouvillian $\hat{L}_0^S = \hat{L}_Z^S(\omega_s) + \hat{L}_{ZFS}^S$ and the relaxation operator $\hat{R}_{ZFS}^{S(T)}$ representing the transient ZFS relaxation mechanism (if $\omega_{ZFS}^T \tau_D \ll 1$):

$$\hat{M}_{ESR} = -i\hat{L}_Z(\omega_s) - i\hat{L}_{ZFS}^S + \hat{R}_{ZFS}^{S(T)}(\omega_s) - i\omega\hat{1} \quad (10)$$

Then, the evaluation of the ESR lineshape should be quite straightforward, even though we have to include the static ZFS. For this purpose, one has to calculate the projection vector $[S_{-1}^1]$ containing the expansion coefficients of the electron spin operator S_{-1} into the Liouville basis constructed from the eigenvectors of the main Hamiltonian H_0^S . The eigenvectors are given as combinations of the Zeeman functions $\{|m_s\rangle\}$ mixed up due to the static ZFS contributing to the main

Hamiltonian, which determines the energy level structure of the system. In consequence, the representations of the operators S_x and S_z can contain some common elements, $|m_s\rangle\langle m'_s|$. This implies that the spin-spin and spin-lattice relaxation processes cannot be treated as independent processes. Thus, one can expect some effects of the spin-lattice electron spin relaxation on the ESR spectra, and this causes considerable complications. Despite the limiting cases of very slow molecular tumbling (when the relative orientation of the static ZFS tensor and the laboratory frame is fixed) and of fast molecular tumbling (that $\omega_{ZFS}^s \tau_R \ll 1$, for instance for water solution of transition metal ions) one cannot describe the electron spin dynamics by a relaxation operator if the static ZFS is present. It brings us to the conclusion that, in fact, we are able to describe analytically the ESR spectra for few limiting cases: when the fluctuations of the orientation of the static ZFS tensor are very fast or when the static ZFS is very weak. It is somewhat difficult to accept so strong theoretical restrictions regarding so fundamental experimental results like ESR spectra. These restrictions do not concern the treatment presented in this paper. Examples of comparisons between ESR lineshape calculated by means of the perturbation treatment and the general approach are presented in (Kruk, 2007). In Fig. 4 we present, for illustrative purposes another example of theoretical ESR lines obtained within the perturbation treatment (under conditions which justify its applicability) and by means of the general theory.

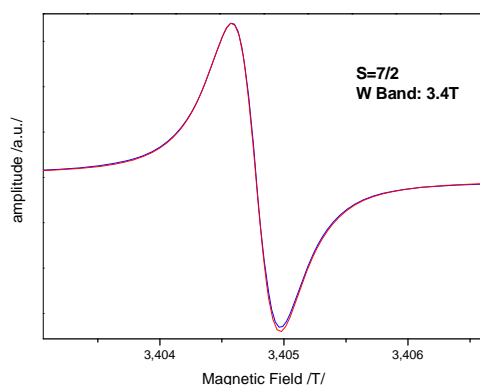


Fig. 4. ESR spectra calculated using the slow motion theory (blue line) and the perturbation theory (red line), $D_s=0.0\text{cm}^{-1}$, $\tau_R=100\text{ps}$, $D_I=0.03\text{cm}^{-1}$, $\tau_D=20\text{ps}$

CONCLUSIONS

The theory of ESR lineshape outlined in this paper is valid for arbitrary interaction strengths and rates of

isotropic reorientation. Even though one cannot explicitly define the electron spin relaxation operator (and, in consequence, electron spin relaxation times), the spectral density function $s_{-1,-1}(\omega)$ describing the lineshape has a well defined meaning. The discussed treatment has a broad application range, especially for biological systems, like for example metalloproteins.

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