Field Dependent Electron and Quadrupole Spin Relaxation: A Unified Treatment

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This article reviews recent theoretical treatments of field dependent relaxation processes in complex systems containing mutually coupled dipolar, quadrupole, and electron spins. The presented approaches are based on an analogy between the Hamiltonian formalisms for quadrupole and zero field splitting interactions. Limitations of the presented treatments, resulting from the validity conditions of the second-order perturbation theory are discussed in detail.

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1. Introduction

Modern NMR experimental techniques give a possibility to observe various dynamic effects in complex systems containing different types of spins. In particular, field dependent relaxation experiments can provide a lot of information on spin interactions and dynamic properties of such systems. Nevertheless, to profit from the advanced experimental methodology one needs appropriate, complete, theoretical models.

In this paper we aim for presenting a review of recent theoretical treatments of field dependent relaxation processes caused by various motional processes and involving different kinds of mutually coupled spins. The theoretical models are quite general and therefore they can be applied to a variety of spin systems characterized by different motional conditions.

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In the first part of this paper we focus attention on field dependent relaxation of quadrupole and electron spins of $S \geq 1$. If the spins are placed in a molecular surrounding of a rather low symmetry, they exhibit a non-zero averaged quadrupole coupling or zero field splitting (ZFS), respectively. However, various dynamic processes occurring in the spin systems cause fluctuations (a spread) of the quadrupole (ZFS) tensor around the averaged value. The averaged interactions have a profound effect (particularly at low magnetic field) on energy level structures of the quadrupole (electron) spins, while their fluctuating counterparts cause relaxation processes within the energy levels. Since the quadrupole coupling as well as the zero field splitting are one-spin interactions expressed in terms of second-rank tensor operators, there are deep formal analogies between the two spin systems.

In the second part we are concerned with spin systems containing nuclear spins of $I = 1/2$ coupled by dipole–dipole interactions to quadrupole (electron) spins of $S \geq 1$. Such systems are very demanding from the point of view of a proper theoretical treatment, however very attractive due to quite unique effects of the field dependent S spin dynamics on the I spin relaxation. The quadrupole (ZFS) interactions influence magnetic field dependences of the dipolar relaxation of the I spin, by affecting transitions frequencies of the entire $I-S$ spin system, while the relaxation processes of the quadrupole (electron) spin contribute to time fluctuations of the dipole-dipole coupling in a manner similar to other stochastic processes, like for example rotational motion or exchange dynamics.

Finally, we discuss in detail validity regimes of the presented models.

We hope that this review will turn out to be useful for NMR community using relaxation studies as a tool for understanding dynamic processes in complex spin systems.

2. Quadrupole coupling and zero field splitting — the Hamiltonian formalisms

Nuclei with spin quantum numbers, S, greater than $1/2$ have a non-spherical charge distribution, which results in a nuclear quadrupole moment. The nuclear quadrupole moment, eQ, of a nucleus interacts with the electric field gradient at the nucleus site. This interaction is described by the Hamiltonian [1–3]:

$$H_Q(S) = \frac{1}{2}\sqrt{\frac{3}{2}}\frac{a_Q}{S(2S+1)}\sum_{m=-2}^{2}(-1)^m A_m T_{2,-m}(S),\tag{1}$$

where $T_{2,-m}(S)$ are components of the rank two-spin tensor operator, defined as $T_{2,0}(S) = \frac{1}{\sqrt{6}}\left[3S_z^2 - S(S+1)\right]$, $T_{2,\pm 1}(S) = \mp\frac{1}{2}\left(S_z S_\pm + S_\pm S_z\right)$, $T_{2,\pm 2}(S) = \frac{1}{2}S_\pm S_\pm$. The quadrupole coupling constant is defined as $a_Q = e^2 qQ/\hbar$, where the symbols have the usual meaning. The A_m functions are defined in the principal axis system of the electric field gradient tensor, referred to as the molecular frame (M). They have the form $A_0^{(M)} = 1$, $A_{\pm 1}^{(M)} = 0$, $A_{\pm 2}^{(M)} = \eta/\sqrt{6}$, where η is the asymmetry

parameter. Employing the well-known transformation rules [4] for tensor operator components one can express the A_m quantities (and in consequence the quadrupole Hamiltonian) in an arbitrary reference frame, particularly in the laboratory one, by the relation $A_m^{(L)} = \sum_{k=-2}^{2} A_k^{(M)} D_{k,m}^2(\Omega_{ML})$. The second-order Wigner rotation matrices, $D_{k,m}^2(\Omega_{ML})$, with the Euler angles Ω_{ML} describe the orientation of the molecular frame with respect to the applied magnetic field. Zero field splitting interactions can have different physical origins, depending on the spin system. In the case of transition metal complexes it is due to second order effects in the spin–orbit coupling; the S manifold is split due to the indirect interaction between unpaired electrons through the spin–orbit coupling [5–8]. For systems such as radicals, a direct dipole–dipole interaction between the unpaired electrons creates the ZFS. The formal expression for the ZFS Hamiltonian is, however, the same irrespective of the physical origin of this interaction, and can be written in full analogy to the quadrupole Hamiltonian [5–8]:

$$H_{ZFS}(S) = \sqrt{\frac{2}{3}} D \sum_{m=-2}^{2} (-1)^m V_m T_{2,-m}(S) \tag{2}$$

with the corresponding spatial tensor components defined in the molecular frame (in this case the principal axis system of the ZFS interaction is defined as the molecular axis system) as: $V_0^{(M)} = 1$, $V_{\pm 1}^{(M)} = 0$, $V_{\pm 2}^{(M)} = (4/\sqrt{6})E/D$. The parameters D and E describe the axial and rhombic components of the ZFS. Looking at Eq. (1) and Eq. (2) one can conclude that the representations of the quadrupole and the ZFS interactions are equivalent. One can easily establish a line of analogy between the two interactions by replacing formally the quadrupole parameters by their ZFS counterparts $D \rightarrow \frac{3}{4} \frac{a_Q}{S(2S-1)}$ and $E \rightarrow \frac{1}{4} \eta \frac{a_Q}{S(2S-1)}$. The static ZFS has an axial symmetry if the ligand field is tetragonal or trigonal. If the symmetry of the ligand field is reduced further, then the rhombic terms appear in the ZFS tensor.

3. Analogies between electron and quadrupole spin systems

An arbitrary spin interaction, described by Hamiltonian $H(t)$, can be expressed as a sum of two components: $H(t) = \langle H(t) \rangle + (H(t) - \langle H(t) \rangle)$. The first term represents an averaged part of the considered interaction: $\langle H(t) \rangle \equiv H_0$, while the second one describes stochastic fluctuations of the $H(t)$ Hamiltonian around its averaged value. If an electron or a quadrupole spin $S \geq 1$ is placed in a low-symmetry environment, one must expect a large averaged ZFS or a large averaged quadrupole coupling, respectively. In a molecular (molecule fixed) frame these interactions are time-independent. In particular, one can treat the principal axis system of these interactions as a molecular frame. If we decide to associate the molecular frame with different interactions (for instance one can choose a dipole–dipole axis as a molecular axis) or symmetry properties of the considered molecule, the principal axis system of the averaged quadrupole (ZFS) interaction does not

coincide with the molecular frame, but remains fixed with respect to it. Therefore, the averaged, time-independent (in a molecular frame) ZFS interaction is referred to as the static ZFS, $H_{\mathrm{ZFS}}^{\mathrm{S}}$ in the literature. Stochastic fluctuations of the ligand framework or the local crystal field lead to a spread of the ZFS interaction around its averaged value. The deviation between the momentary ZFS and its averaged (static) value is called the transient ZFS, $H_{\mathrm{ZFS}}^{\mathrm{T}}(t)$ in the literature [7–11]. In analogy, an averaged electric field gradient (EFG) creates a time-independent (static) quadrupole coupling, H_Q^{S}, while local fluctuations of the EFG lead to a transient quadrupole interaction, described by a time-dependent Hamiltonian, $H_Q^{\mathrm{T}}(t)$. It is very important to realize that the decomposition of these interactions into the static (time-independent) and transient (time-dependent) parts has been performed in a molecule-fixed frame. From the viewpoint of the molecule-fixed frame, the static and transient parts represent the mean and the spread, respectively, of the total interactions. The static interactions are time-independent in a molecular frame, while the transient ones are not, because they fluctuate relative to that frame. In particular, the static quadrupole coupling is defined in the principal axis system of the averaged electric field gradient tensor and remains unchanged in time in this reference frame, whereas the transient quadrupole Hamiltonian describes (in the same reference frame) stochastic deviations of the total quadrupole interaction from its averaged value. The transient interactions possess also their own principal axis systems; however, they are not fixed in the molecule. A pictorial view of the three relevant reference systems: the laboratory and the molecular frames and the principal axis system of the transient ZFS (quadrupole) interaction, is presented in Fig. 1. The averaged (static) interactions are time-independent in a
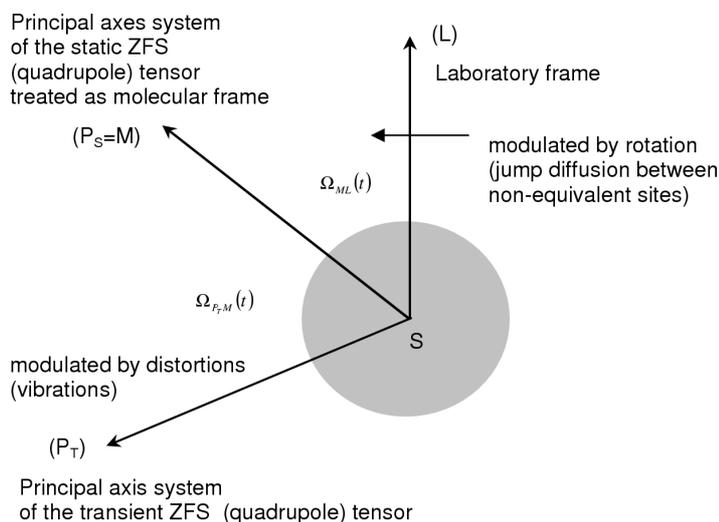

Fig. 1. Relative orientations of the principal axis system of the static and transient components of the ZFS and the quadrupole coupling with respect to the laboratory frame.

molecular frame; however they can fluctuate in time with respect to the laboratory system. Both the components of the ZFS (quadrupole) coupling have profound effects on the electron (quadrupole) spin dynamics. The role of these interactions depends on their strengths (amplitudes) and motional conditions characterizing the systems. In fact, the timescale of the modulations of the averaged quadrupole and ZFS interactions with respect to the laboratory frame determines the physical picture of the quadrupole- and respectively the electron spin dynamics. Depending on the system under interest, various types of motion can be responsible for the fluctuations in the orientation of the molecular frame (the principal axis system of the electric field gradient tensor or the ZFS tensor). The relative orientation of the laboratory and molecular frames can change in time due to rotational motion of the molecule carrying the S spin [11–15]. In solid state systems spins S can move between non-equivalent lattice sites characterized by a different local crystal field due to, for example, exchange motion of the particles (ions, nuclei). The jump diffusion mediates, in this case, the orientation of the principal axis systems of the quadrupole or the ZFS couplings at the temporary position of the S spin.

In this paper we shall discuss various timescales of the motion affecting the relative orientation of the molecular and laboratory frames. Nevertheless, it will turn out that it is possible to describe the S spin dynamics in terms of well--defined relaxation rates only for a few limiting cases. It is so due to restricted validity regimes of the second-order perturbation theory. Relaxation theories are based on a perturbation solution of the Liouville equation [1–3, 16–19]. The perturbation theory requires an unambiguous decomposition of the total Hamiltonian describing the entire spin system into a main and a perturbing part, H_0 and $H_1(t)$, respectively. The Hamiltonians have to fulfill the two main conditions: $|H_1\tau_{\rm c}| \ll 1$ (where $\tau_{\rm c}$ is the correlation time describing the timescale of the fluctuations of this interaction relative to the principal axis system of the main Hamiltonian H_0) and $|H_1\tau_{\rm c}| \ll |H_0/H_1|$, referred to as the Redfield condition and the secular approximation condition, respectively. The Redfield condition implies that the resulting relaxation timescale is much slower than the fluctuations causing the relaxation. If the requirements are not fulfilled one cannot describe the spin dynamics in terms of well-defined, time-independent relaxation rates.

4. Electron and quadrupole spin relaxation

This section is concerned with a description of relaxation processes in systems characterized by non-zero averaged interactions of the second order, like the ZFS and the quadrupole coupling. We shall take full advantage of the common representation of both the interactions and apply the Redfield relaxation theory [1–3, 17–19], considering with caution its validity conditions.

The most favorable case is one of very slow molecular tumbling, jump diffusion, or any other type of motion, which can mediate the relative orientation of the molecular and laboratory frames. Under these conditions the two frames

are obviously fixed with respect to each other. As it has been pointed out in the previous section, the perturbation theory requires one to divide unambiguously the total Hamiltonian including all interactions relevant for the system under interest into main (time-independent) and perturbing parts. If the molecular frame does not fluctuate with respect to the laboratory axis, this requirement can be easily fulfilled for an arbitrary magnetic field. Then the energy level structure of the S spin is determined by a combination of the Zeeman interaction, $H_Z(S)$, and the static components of the second order couplings, $H^S_{ZFS}(S)$ or $H^S_Q(S)$. Index S indicates that we deal with the static (averaged) parts of the quadrupole coupling and the zero field splitting; it should not be confused with the spin labeling. From now on we shall denote both of the interactions as $H^S_2(S)$ (index (2) comes from their representation by the second-order tensors). In fact, because of the common Hamiltonian formalism, in order to describe the S spin dynamics one does not need to distinguish between the two interactions. Thus, the main Hamiltonian, $H_0(S)$, represented in the laboratory frame ($H_0^{(L)}(S)$), takes the following form [12, 14]:

$$H_0^{(L)}(S) = H_Z^{(L)}(S) + H_2^{S(L)}(S) =$$

$$\omega_S S_z + \sum_{m=-2}^{2} (-1)^m F_m^{S(L)}(\Omega_{ML}) T_{2,-m}(S). \tag{3}$$

The functions $F_m^{S(L)}(\Omega_{ML})$ can be associated with the quadrupole coupling; in this case they are equal to $F_m^{S(L)}(\Omega_{ML}) = \frac{1}{2}\sqrt{3/2}a_Q^S \sum_{k=-2}^{2} A_k^{S(M)} D^2_{k,m}(\Omega_{ML})$ (Eq. (1)), or with the static ZFS interaction $F_m^{S(L)}(\Omega_{ML}) = \sqrt{2/3}D_S \sum_{k=-2}^{2} V_k^{S(M)} D^2_{k,m}(\Omega_{ML})$ (Eq. (2)). The quantities $A_k^{S(M)}$ and $V_k^{S(M)}$ contain the parameters describing the static parts of these interactions, i.e. $A_0^{S(M)} = 1$, $A_{\pm 1}^{S(M)} = 0$, $A_{\pm 2}^{S(M)} = \eta_S/\sqrt{6}$, while $V_0^{S(M)} = 1$, $V_{\pm 1}^{S(M)} = 0$, $V_{\pm 2}^{S(M)} = (4/\sqrt{6})E_S/D_S$. In the limiting case of a low magnetic field when $|H^S_{ZFS}(S)| \gg |H_Z(S)|$ or $|H^0_Q(S)| \gg |H_Z(S)|$, the energy level structure of the S spin is determined by the second-order interactions, $H^S_{ZFS}(S)$ or $H^S_Q(S)$, respectively. On the contrary, if the applied magnetic field is high enough to fulfill the condition $|H_Z(S)| \gg |H^S_Q(S)|$ or $|H_Z(S)| \gg |H^S_{ZFS}(S)|$, the S spin exhibits the Zeeman energy levels. In general, the energy levels E_α of the S spin depend on the orientation of the principal axis system of the $H^S_{(2)}(S)$ interaction with respect to the external magnetic field. They can be obtained as eigenvalues of the matrix representation of the main Hamiltonian, $H_0^{(L)}$, in the basis $\{|m_S\rangle\}$ constructed from the Zeeman functions; m_S denotes the magnetic quantum number of the S spin. In consequence, the corresponding eigenfunctions, $|\psi_\alpha\rangle$, can be expressed as linear combinations of the Zeeman basis functions: $|\psi_\alpha^S\rangle = \sum_{r=1}^{2S+1} c_{\alpha,m_S}(\Omega_{ML})|m_S\rangle$, where the specific, angular dependent coefficients, $c_{\alpha,m_S}(\Omega_{ML})$, result from diagonalization of the Hamiltonian matrix. We are interested in explicit, closed form expressions for the individual

relaxation rates connecting time evolution of the coherences (populations), $\rho_{\alpha\alpha'}^{S}$ and $\rho_{\beta\beta'}$. The $\rho_{\alpha\alpha'}$ coherences are represented by the elements of the Liouville basis, $\{|\psi_\alpha\rangle\langle\psi_{\alpha'}|\}$, generated by the eigenfunctions of the main Hamiltonian. They are associated with the Zeeman coherences, $\rho_{m_S m_S'} \equiv |m_S\rangle\langle m_S'|$, by the relationship $|\psi_\alpha\rangle\langle\psi_{\alpha'}| = \sum_{r,r'=1}^{2S+1} c_{\alpha,m_S}(\Omega_{\mathrm{ML}}) c_{\alpha',m_S'}^*(\Omega_{\mathrm{ML}})|m_S\rangle\langle m_S'|$ [12, 14, 16]. The well-known Redfield formula [1–3, 17–19]:

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha\beta}) + J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha'\beta'}) - \delta_{\alpha'\beta'} \sum_\gamma J_{\alpha\gamma\beta\gamma}(\omega_{\gamma\beta})$$

$$- \delta_{\alpha\beta} \sum_\gamma J_{\beta'\gamma\alpha'\gamma}(\omega_{\beta'\gamma}) \tag{4}$$

gives the relaxation rates $R_{\alpha\alpha'\beta\beta'}$ in terms of the spectral densities $J_{\alpha\alpha'\beta\beta'}(\omega)$ determined by corresponding matrix elements of the relaxation Hamiltonian $H_1(t)$:

$$J_{\alpha\alpha'\beta\beta'}^S(\omega) = \int_0^\infty \langle\langle\psi_\alpha^S|H_1(0)|\psi_{\alpha'}^S\rangle \langle\psi_\beta^S|H_1(t)|\psi_{\beta'}^S\rangle\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t, \tag{5}$$

where the external brackets $\langle\rangle$ denote the ensemble average. The representation of the perturbing interaction requires some caution. The perturbation theory requires the perturbing Hamiltonian, $H_1(t)$, to be expressed in the reference frame associated with the main interaction. However, the quantization axis of the S spin depends on the relation between the amplitudes of the Zeeman coupling and of the second-order interaction. In the present case the relaxation mechanism for the electron spin is provided by the transient ZFS, while time fluctuations of the electric field gradient create the quadrupole relaxation mechanism, associated with the transient quadrupole coupling. Therefore, in low magnetic field we should consider the fluctuations of the transient interactions with respect to the principal axis systems of their static counterparts, while in high magnetic field we should ask about the timescale of the fluctuations relative to the laboratory frame. In addition, we have to pass through the intermediate regime of the magnetic field, when the Zeeman coupling and the static second-order interaction compete. It implies that in principle we should continuously alter the Hamiltonian of the perturbing interactions when the magnetic field changes, transforming it to the appropriate reference frame. Such a treatment would lead to quite cumbersome calculations. Fortunately, we can profit at this stage from the fact that the molecular and the laboratory frames are fixed with respect to each other and therefore the fluctuations of the transient interactions relative to both of them are characterized by exactly the same time constant. Independently of the physical origin of the time modulations of the electric field gradient tensor or the ligand (crystal) field, the perturbing Hamiltonian, $H_1(t)$, can be written in terms of the second-rank tensor components, $T_{2,-m}(S)$, and the corresponding time-dependent quantities, $F_m^{\mathrm{T}}(t)$, representing the transient (fluctuating) parts of the quadrupole or the ZFS interaction $H_1(t) = \sum_{m=-2}^2 (-1)^m F_m^{\mathrm{T}}(t) T_{2,-m}(S)$. The Hamiltonians

describing the transient interactions are defined in their own principal axis systems (P_T) (not fixed in the molecule) by the time independent quantities, $F_m^{T(P_T)}$. They can be defined in full analogy to the functions describing the static interactions, i.e. for the quadrupole coupling $F_m^{T(P_T)} = A_m^{T(P_T)}$, where $A_0^{T(P_T)} = 1$, $A_{\pm 1}^{T(P_T)} = 0$, $A_{\pm 2}^{T(P_T)} = \eta_T/\sqrt{6}$, and, for the ZFS interaction $F_m^{T(P_T)} = V_m^{T(P_T)}$ where $V_0^{T(P_T)} = 1$, $V_{\pm 1}^{T(P_T)} = 0$, $V_{\pm 2}^{T(P_T)} = (4/\sqrt{6})E_T/D_T$. The time-dependent functions, $F_m^T(t)$, result from the transformation of $F_m^{T(P_T)}$ from the principal axis system of the transient interactions (P_T) to the reference frame determined by the main Hamiltonian (P_0) via the set of the Euler angles $\Omega_{P_T P_0}(t)$. The angles describe the relative orientation of these frames, which varies stochastically in time $F_m^T(t) = \sum_{k=-2}^{2} F_k^{T(P_T)} D_{k,m}^2[\Omega_{P_T P_0}(t)]$. In the limiting cases of the low and high magnetic field, the (P_0) frame coincides with the principal axis system of the averaged quadrupole (ZFS) interactions or with the laboratory (L) frame, respectively.

The above definition of the $F_m^T(t)$ quantities is based on a very simple motional model assuming that their amplitudes do not undergo any time fluctuations (this model is referred to as "pseudorotational model" [8, 9, 11–16]). Taking into account that the interactions are affected by damped vibrations in crystal lattices or molecules, such a treatment is an apparent simplification. There are more advanced and realistic models present in the literature. Particularly, in [20, 21] the ZFS tensor has been expressed in terms of normal coordinates describing the internal geometry of a paramagnetic complex carrying a transition metal ion. Within this model the $V_m^{T(P_T)}$ functions depend on the geometry of the complex and describe the instantaneous magnitude of the transient ZFS. They are given as a Taylor expansion of the quantities D and E in a set of normal coordinates characteristic of the complex under interest. This motional model is much more demanding from the computational point of view for two reasons. The first one is that one must know the responses of the D and E tensor components with respect to the changes in the individual normal coordinates q_i ($\partial D/\partial q_i, \partial E/\partial q_i$). The second very important problem is whether the vibrational degrees of freedom can be treated classically [20] or one has to take into account the quantum nature of the motion [21]. Motional models explaining local time fluctuations of the electric field gradient and the crystal field are a very challenging and complicated issue by itself. It is not, however, discussed in great detail in what follows, because our main concern is connected with the relaxation processes. For this purpose it is enough to deal with the general representation of the perturbing interaction, not employing any explicit expressions for the $F_m^T(t)$ quantities, depending on the assumed motional model.

The spectral densities $J_{\alpha\alpha'\beta\beta'}^S(\omega)$ (index S denotes here spin), introduced by Eq. (5), can be expressed by corresponding quantities involving the matrix elements of the perturbing interaction taken between the Zeeman states $|m_S\rangle$ [14, 16]:

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \sum_{m_S,m'_S} c^*_{\alpha m_S} c_{\alpha'm'_S} c^*_{\beta m'_S} c_{\beta'm_S}$$

$$\times \int_0^\infty \langle\langle m_S|H_1(0)|m'_S\rangle\,\langle m'_S|H_1(t)|m_S\rangle\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t. \tag{6}$$

This expression comes from the relationship between the eigenvectors $|\psi_\alpha^S\rangle$ and the Zeeman functions $|m_S\rangle$, which gives us the relation between the matrix elements of the perturbing Hamiltonian taken in the two bases $\langle\psi_\alpha^S|H_1^{(\mathrm{L})}|\psi_{\alpha'}^S\rangle = \sum_{r,r'=1}^{2S+1} c^*_{\alpha m_S} c_{\alpha'm'_S}\langle m_S|H_1|m'_S\rangle$. Aiming for general formulations it is very useful to separate the spin and the spatial components of the perturbing Hamiltonian $H_1(t)$ and express the spectral densities $J^S_{\alpha\alpha'\beta\beta'}(\omega)$ by the quantities $J^S_m(\omega) = \int_0^\infty \langle F^*_m(0)F_m(t)\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t$ dependent only on the applied motional model

$$\int_0^\infty \langle\langle m_S|H_1(0)|m'_S\rangle\,\langle m'_S|H_1(t)|m_S\rangle\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t =$$

$$\sum_{m=-2}^2 |\langle m_S|T_{2,-m}|m'_S\rangle|^2\, J^S_m(\omega). \tag{7}$$

The matrix elements, $\langle m_S|T_{2,-m}(S)|m'_S\rangle$, of the tensor components $T_{2,-m}$ have a non-zero value only if $\Delta m_S = m$, where Δm_S is the difference between the magnetic quantum number of the spin S for the Zeeman eigenstates $|m_S\rangle$ and $|m'_S\rangle$, i.e. $\Delta m_S = m_S - m'_S$. Setting up Eq. (7) we have taken into account only correlation between quantities F_m of the same order. In the case of the pseudorotational model of the transient interactions it is justified by the orthogonality properties of the Wigner rotation matrices. The motional models presented in [20, 21] do not require to consider cross-correlation terms. Nevertheless, for completeness of the presentation it can be worthwhile to write down a generalized form of Eq. (7), allowing for cross-correlation effects

$$\int_0^\infty \langle\langle m_S|H_1(0)|m'_S\rangle\,\langle m'_S|H_1(t)|m_S\rangle\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t =$$

$$\sum_{m,m'=-2}^2 |\langle m_S\,|T_{2,-m}|\,m'_S\rangle\,\langle m'_S\,|T_{2,-m'}|\,m_S\rangle|\, J^S_{m,m'}(\omega). \tag{7a}$$

Employing the Redfield formula of Eq. (4) one can set up explicit expressions for the individual relaxation rates $R_{\alpha\beta\alpha\beta}$ and $R_{\alpha\alpha\beta\beta}$ [14, 16]:

$$R_{\alpha\beta\alpha\beta}(\Omega_{\mathrm{ML}}) = 2\xi_{\alpha\beta}(\Omega_{\mathrm{ML}})J(0) - \sum_{\gamma=1}^{2S+1} \xi_{\gamma\alpha}(\Omega_{\mathrm{ML}})J(\omega_{\gamma\alpha})$$

$$- \sum_{\gamma=1}^{2S+1} \xi_{\gamma\beta}(\Omega_{\mathrm{ML}})J(\omega_{\gamma\beta}), \tag{8}$$

$$R_{\alpha\alpha\beta\beta}(\Omega_{\mathrm{ML}}) = \xi_{\alpha\beta}(\Omega_{\mathrm{ML}})J(\omega_{\alpha\beta}). \tag{9}$$

The orientation dependent coefficients

$$\xi_{\alpha\beta}(\Omega_{\mathrm{ML}}) = \sum_{n=-2}^{2}\left(\sum_{r,r'}^{2S+1}\left|c_{\alpha m_S}^{*}c_{\beta m_S'}\right|^2(\Omega_{\mathrm{ML}})\left|\langle m_S|T_{2,n}(S)|m_S'\rangle\right|^2\right)$$

come from Eq. (7) substituted into Eq. (6). The remaining relaxation rates $R_{\alpha\alpha\alpha\alpha}(\Omega_{\mathrm{ML}})$ are given as the sum over the $R_{\alpha\alpha\beta\beta}(\Omega_{\mathrm{ML}})$ elements: $R_{\alpha\alpha\alpha\alpha}(\Omega_{\mathrm{ML}}) = -\sum_{\beta\neq\alpha}R_{\alpha\alpha\beta\beta}(\Omega_{\mathrm{ML}})$. We have assumed in the expressions of Eqs. (8), (9) that the spectral densities $J_m(\omega)$ are independent of the order of the involved transition, i.e. $J_m(\omega) = J(\omega)$. It is particularly true for the above described, simplest model of the stochastic fluctuations of the quadrupole and the ZFS tensors. In this case the spectral densities $J_m(\omega)$ take the form $J_m(\omega) = \frac{1}{5}\frac{\Delta_{\mathrm{T}}^2\tau_{V(Q)}}{1+\omega^2\tau_{V(Q)}^2}$, where the amplitude of the transient ZFS (or the transient quadrupole coupling) is defined as $\Delta_{\mathrm{T}} = \frac{2}{3}D_{\mathrm{T}}^2 + 2E_{\mathrm{T}}^2$ (or $\Delta_{\mathrm{T}} = \frac{3(a_Q^{\mathrm{S}})^2}{8S(S+1)}\left(1+\frac{\eta_{\mathrm{S}}}{3}\right)$). The correlation times τ_V and τ_Q reflect the timescale of the fluctuations of the ZFS and the quadrupole interaction.

Finishing this part of the considerations we wish to give more attention to the conditions under which the already presented description can be applied. For clarity reasons we shall formulate them explicitly. First of all, the interactions causing the relaxation processes must fulfill the Redfield condition $\left|H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V\right| \ll 1$ or $\left|H_Q^{\mathrm{T}}\tau_Q\right| \ll 1$. The next requirement, referred to as the secular approximation condition, concerns the relation between the main Hamiltonian H_0 and the perturbing one: $|H_0/H_{\mathrm{ZFS}}^{\mathrm{T}}| \gg |H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V|$ or $|H_0/H_Q^{\mathrm{T}}| \gg |H_Q^{\mathrm{T}}\tau_Q|$. At low magnetic field, the main Hamiltonian is provided by the static parts of the second-order interactions (the static ZFS or the static quadrupole coupling). Therefore, the perturbation theory, when applied in the low field limit, requires the relationships $|H_{\mathrm{ZFS}}^{\mathrm{S}}/H_{\mathrm{ZFS}}^{\mathrm{T}}| \gg |H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V|$ or $|H_Q^0/H_Q^{\mathrm{T}}| \gg |H_Q^{\mathrm{T}}\tau_Q|$ to be satisfied. If the magnetic field increases, the Zeeman coupling starts to play a noticeable role and supports the static ZFS to fulfill the relation $|(H_{\mathrm{ZFS}}^{\mathrm{S}} + H_{\mathrm{Z}})/H_{\mathrm{ZFS}}^{\mathrm{T}}| \gg |H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V|$ (it concerns of course also the quadrupole interaction). Finally, the Zeeman coupling becomes strong enough, to fulfill the relation $|H_{\mathrm{Z}}/H_{\mathrm{ZFS}}^{\mathrm{T}}| \gg |H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V|$ by itself. The explicit expressions determining the validity regime of the relaxation theory indicate that some complications arise, for example, when the transient components of the ZFS or the quadrupole interactions momentarily are larger than their static counterparts, because then the energy levels of the S spin can, at each instant, be considered as being determined by the transient rather than the static part [22].

Until now we have discussed the case of the static parts of the second-order interactions being fixed in the laboratory frame. When the relative orientation of the molecular and laboratory frames changes in time due to, for example, fast molecular tumbling or jump diffusion, we are able to describe the dynamic of the S spin in terms of well-defined relaxation rates only in the limiting magnetic field

regimes [11, 15]. In the high field limit, when the Zeeman coupling is much larger than the averaged ZFS or the averaged quadrupole interaction, the electron spin or the quadrupole spin, respectively, precesses around the external magnetic field. Thus, the Zeeman Hamiltonian is considered as the time-independent Hamiltonian describing the energy level structure, independently of the timescales of the dynamic processes occurring in the spin system. However, now there are two relaxation channels for the S spin; the first one related to the transient components of the second-order interactions modulated, for example, by lattice vibrations or distortions in the molecular geometry, while the second one is provided by the static components of these interactions modulated, for example, by the molecular tumbling. One should not be confused at this moment by the statement that a "static" interaction provides a relaxation mechanism. We would like to point out that the terminology "static quadrupole (ZFS)" originates from the fact that these interactions do not fluctuate in time (are static) in a molecular frame. In the present case we consider both the components (the static and the transient ones) with respect to the laboratory frame. Due to the molecular rotation the relative orientation of the principal axis systems of the averaged (static) interactions and the laboratory frame fluctuates stochastically in time, and therefore the averaged interactions do provide a relaxation mechanism. It is very important in this context to consider carefully possible correlations between the dynamic processes mediating the transient and the static interactions, respectively. They have essentially a different physical origin and therefore, even if they occur on a similar timescale, one can treat them as uncorrelated. It implies that there is no interference between the two relaxation mechanisms. In fact, the distortional (vibrational) motion is usually on a very rapid timescale (usually a few ps) relative to molecular reorientation or any kind of exchange dynamics. Since in the high field limit the Zeeman basis $\{|m_S\rangle\}$ is the eigenbasis of the main Hamiltonian, the expressions for the individual relaxation rates connecting the evolution of the populations of the Zeeman energy levels, $\rho_{rr} \equiv |r\rangle\langle r|$, or the coherences, $\rho_{rr'} \equiv |r\rangle\langle r'|$ ($|r\rangle \equiv |m_S\rangle, |r'\rangle \equiv |m_S'\rangle$), are particularly simple. They are just given directly by Eqs. (8), (9) applied to the Zeeman energy level structure of the spin under interest. Nevertheless, some caution must be exercised regarding the perturbing Hamiltonian $H_1(t)$. It contains, in the present case, the laboratory representation of the total second-order interactions, decomposed into the static and the transient parts: $H_1(t) = H_{(2)}^{\mathrm{S(L)}} + H_{(2)}^{\mathrm{T(L)}}$. The exact form of the first Hamiltonian, $H_{(2)}^{\mathrm{S(L)}}$, has been provided in Sect. 2. To point out that the static interactions provide now the relaxation mechanism due to stochastic time fluctuations of their principal axis systems it is appropriate to write explicitly that $\Omega_{\mathrm{ML}} = \Omega_{\mathrm{ML}}(t)$. At this moment one should realize that the proper, complete form of the Hamiltonian $H_{(2)}^{\mathrm{T(L)}}$ results from a two-step transformation. First, the transient ZFS (or the transient quadrupole coupling) defined in its own principal axis system ($\mathrm{P_T}$) should be transformed to the molecular frame (M) through the

set of the Euler angles $\Omega_{\mathrm{P_T M}}(t)$ affected by the vibrational (distortional) motion. Next, the molecular frame representation of the transient interactions should be transformed into the laboratory frame (L) employing the second set of the Euler angles $\Omega_{\mathrm{ML}}(t)$ modulated, for example, by the molecular tumbling. Therefore, the Hamiltonian $H_{(2)}^{\mathrm{T(L)}}$ takes the following form:

$$H_{(2)}^{\mathrm{T(L)}} = \sum_{m=-2}^{2} (-1)^m F_m^{\mathrm{T(L)}} T_{2,-m} =$$

$$\sum_{m=-2}^{2} (-1)^m \left[\sum_{n=-2}^{2} \sum_{k=-2}^{2} F_k^{\mathrm{T(P_T)}} D_{k,n}^2 \left(\Omega_{\mathrm{P_T M}} \right) D_{n,m}^2 \left(\Omega_{\mathrm{ML}} \right) \right] T_{2,-m}. \quad (10)$$

In consequence, the spectral density functions $J_m(\omega)$ enclose the static and the transient contributions to the relaxation $J_m(\omega) = J_m^S(\omega) + J_m^{\mathrm{T}}(\omega)$. The first term has been already defined: $J_m^S(\omega) = \frac{1}{5} \frac{\Delta_{\mathrm{T}}^2 \tau_{V(Q)}}{1+\omega^2 \tau_{V(Q)}^2}$. However, taking into account the by now described two-step transformation of the transient Hamiltonian $H_{(2)}^{\mathrm{T}}$, the correlation time $\tau_{V(Q)}$ should be modified by including the motional process modulating the angle $\Omega_{\mathrm{ML}}(t)$: $\left(\tau_{V(Q)}' \right)^{-1} = \tau_{V(Q)}^{-1} + \tau_{V_S(Q_S)}^{-1}$. Index S indicates the correlation time characteristic of the fluctuations of the static components of the ZFS or quadrupole couplings with respect to the direction of the applied magnetic field. Because of the formally similar definition of the static and transient interactions, the second term, $J_m^{\mathrm{T}}(\omega)$ can be written in full analogy to the first one, as $J_m^S(\omega) = \frac{1}{5} \frac{\Delta_{\mathrm{S}}^2 \tau_{V_S(Q_S)}}{1+\omega^2 \tau_{V_S(Q_S)}^2}$. In low magnetic field, the precession of the S spin occurs around the principal axis system of the static ZFS or the static quadrupole tensor and the energy level structure of the S spin is determined by these static interactions. In this regime, the transient components modulated by distortional or vibrational motion provide the predominant mechanism of the S spin relaxation. Since the Zeeman coupling is modulated with respect to the molecular frame, for example, by rotational motion, one might consider the Zeeman interaction as a perturbation contributing also to the relaxation.

5. Relaxation of nuclear spins 1/2 via couplings to neighboring quadrupole or electron spin of $S \geq 1$

This section is concerned with relaxation of a dipolar, nuclear spin, $I = 1/2$, caused by a dipole–dipole coupling to an electron or a quadrupole spin relaxing in the already described complicated, field dependent manner. Figure 2 shows a schematic view of such spin systems. We shall take full advantage of the Redfield description of the S spin relaxation, formulated in the previous section.

The idea of this approach is to let the S spin to be a part of a composite lattice for the I spin [8, 9, 11–15, 20–23]. The composite lattice includes quantum mechanical degrees of freedom related to the S spin subsystem as well as classical degrees of freedom. They involve the motions affecting the orientation of the
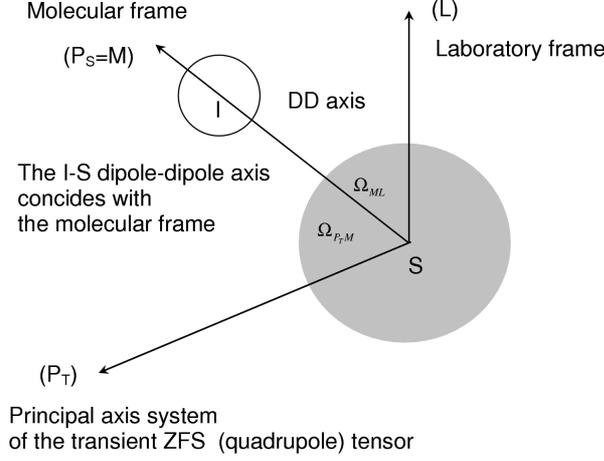
Fig. 2. A schematic illustration of the structure of the $I-S$ spin system.

$I-S$ dipole–dipole axis and the lattice vibrations (distortions) leading to the time fluctuations of the ZFS tensor.

The "ordinary" form of the $I-S$ dipole–dipole Hamiltonian $H_{\mathrm{DD}}^{(\mathrm{L})}(I,S)$ expressed in the laboratory frame is

$$H_{\mathrm{DD}}^{(\mathrm{L})}(I,S) = a_{\mathrm{D}} \sum_{m=-2}^{2} (-1)^m D_{0,m}^2\left(\Omega_{IS}^{\mathrm{L}}\right) T_{2,-m}(I,S), \tag{11}$$

where the components $T_{2,-m}(I,S)$ of the two-spin tensor operator have the form $T_{2,0} = \frac{1}{\sqrt{6}}\left[2I_z S_z - \frac{1}{2}(I_+S_- + I_-S_+)\right]$, $T_{2,\pm1} = \mp\frac{1}{2}\left(I_z S_\pm + I_\pm S_z\right)$, $T_{2,\pm2} = \frac{1}{2}I_\pm S_\pm$, and the dipolar coupling constant is defined as $a_{\mathrm{D}} = \sqrt{6}\frac{\mu_0}{4\pi}\frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3}$ (where r_{IS} is the inter-spin distance), other symbols have their usual meaning. The Euler angles Ω_{IS}^{L} describe the orientation of the $I-S$ dipole–dipole axis with respect to the laboratory frame. Since we intend to treat the spin S as a part of the lattice we have to adjust in an appropriate manner the form of the spin lattice coupling. Therefore, we need to separate in Eq. (11) the part, which is dependent only on the I spin operators from other quantities characterizing now the composite lattice. One can achieve this expressing the second-order $I-S$ tensor operators $T_{-m}^2(I,S)$ in terms of the first-order tensors: I_n^1 and S_n^1 for the I and S spins, respectively [4]. Then the dipole–dipole Hamiltonian becomes

$$H_{\mathrm{DD}}^{(\mathrm{L})}(I,S) = a_{\mathrm{D}}^{IS} \sum_{n=-1}^{1} (-1)^n I_{-n}^1 T_n^{1(\mathrm{DD})} = a_{\mathrm{D}}^{IS} \sum_{n=-1}^{1} (-1)^n I_{-n}^1$$

$$\times \left[\sqrt{5} \sum_{q=-1}^{1} \begin{pmatrix} 2 & 1 & 1 \\ n-q & q & -n \end{pmatrix} S_q^1 D_{0,n-q}^2\left(\Omega_{IS}^{\mathrm{L}}\right) \right], \tag{12}$$

where the last equality gives explicitly the tensor operators $T_n^{1(\mathrm{DD})}$ associated with the lattice. The tensor operators I_n^1 (S_n^1) are related to the angular momentum operators: $P_0^1 = P_z$, $P_{\pm 1}^1 = \frac{1}{\sqrt{2}} P_\pm$, $P = I, S$, while $\begin{pmatrix} 2 & 1 & 1 \\ n-q & q & -n \end{pmatrix}$ are the appropriate 3-j symbols. The two elements of the lattice operators $T_n^{1(\mathrm{DD})}$ describe the main components of the lattice: the degrees of freedom encoded in the Wigner rotation matrices $D_{0,n-q}^2 \left(\Omega_{IS}^{\mathrm{L}} \right)$, modulating "directly" the $I-S$ dipole–dipole interaction, and the S_q^1 operators, which represent the contribution of the S spin system to the fluctuations of the $I-S$ coupling. The dynamics of the S spin has been described in detail in the previous section. The division of the entire system into the spin under interest, I, and the composite lattice is presented in Fig. 3.
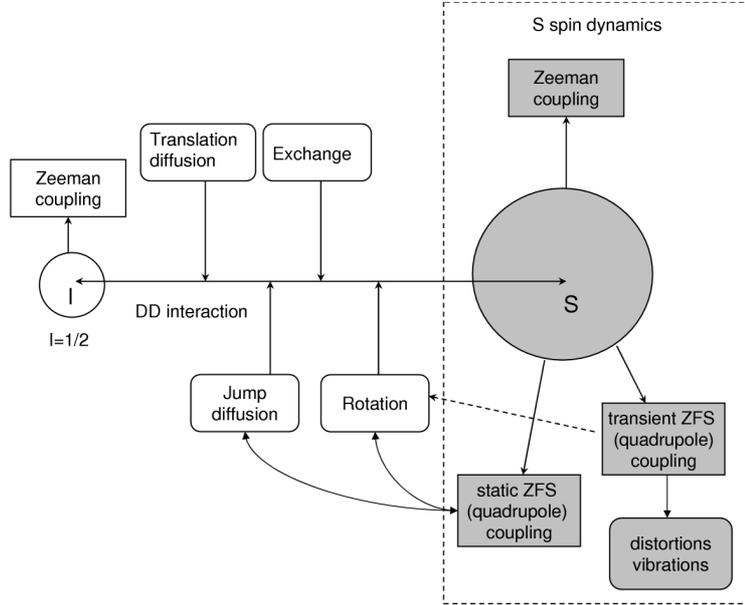

Fig. 3.   A pictorial view of the $I-S$ spin system.

Employing the Redfield relaxation theory with the dipole–dipole coupling of Eq. (12) as the perturbing interaction one can derive formulae for relaxation rates describing evolution of individual magnetization modes and coherences of the I spin. In particular, for $I = 1/2$, the I spin spin–lattice relaxation rate, $R_{1(I \to S)}$ caused by the dipole–dipole interaction to an arbitrary spin S can be obtained from the expression $R_{1(I \to S)} = 2\mathrm{Re}\left[K_{IS}^{\mathrm{DD}}(-\omega_I) \right]$ [8, 9, 11–15, 20–23]. The spectral density, $K_{IS}^{\mathrm{DD}}(-\omega_I)$, is defined as the Fourier transform of the corresponding correlation function $G_{IS}^{\mathrm{DD}}(\tau)$ [8, 9, 11]:

$$K_{IS}^{\mathrm{DD}}(-\omega_I) = \int_0^\infty G_{IS}^{\mathrm{DD}}(t) \exp(-\mathrm{i}\omega_I t)\mathrm{d}t =$$

$$\int_0^\infty \mathrm{Tr}_L \left\{ T_{m'}^{l+} \exp\left(-\mathrm{i}\hat{\hat{L}}_L t\right) T_m^l |\rho_L^{\mathrm{eq}}\right\} \exp(-\mathrm{i}\omega_I t)\mathrm{d}t. \tag{13}$$

With the expression of the components of the lattice tensor operators $T_n^{1(\mathrm{DD})}$, resulting from the dipole–dipole spin–lattice coupling given by Eq. (12), the spectral density $K_{11}^{\mathrm{DD}}(-\omega_I)$ may be written as [8, 9, 11–15, 20–24]:

$$K_{IS}^{\mathrm{DD}}(-\omega_I) = 30 \left(\frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi}\right)^2 \sum_{p,q} \begin{pmatrix} 2 & 1 & 1 \\ 1-q & q & -1 \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ 1-p & p & -1 \end{pmatrix}$$

$$\times \int_0^\infty \mathrm{Tr}_L \left\{ S_q^{1(\mathrm{L})+} \frac{D_{0,1-q}^{2*}\left[\Omega_{IS}^{\mathrm{L}}(t)\right]}{r_{IS}^3(t)} \exp\left(-\mathrm{i}\hat{\hat{L}}_L t\right) S_p^{1(\mathrm{L})} \frac{D_{0,1-p}^2\left[\Omega_{IS}^{\mathrm{L}}(0)\right]}{r_{IS}^3(0)} \rho_L^{\mathrm{eq}}\right\}$$

$$\times \exp(-\mathrm{i}\omega_I t)\mathrm{d}t. \tag{14}$$

The independence of the dynamics of the S spin of the motion modulating "directly" the dipole–dipole interaction leads to the separation of the correlation function $G_{IS}^{\mathrm{DD}}(t)$ into one function involving only the S spin part and another one including the remaining degrees of freedom: $C(t) = \left\langle \frac{D_{0,1-q}^{2*}\left(\Omega_{IS}^{\mathrm{L}}(t)\right)}{r_{IS}^3(t)} \frac{D_{0,1-p}^2\left(\Omega_{IS}^{\mathrm{L}}(0)\right)}{r_{IS}^3(0)} \right\rangle$

[11–15, 20–24]:

$$K_{IS}^{\mathrm{DD}}(-\omega_I) = 30 \left(\frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi}\right)^2 \sum_{p,q} \begin{pmatrix} 2 & 1 & 1 \\ 1-q & q & -1 \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ 1-p & p & -1 \end{pmatrix}$$

$$\times \int_0^\infty C(t) \mathrm{Tr}_S \left\{ S_q^{1(\mathrm{L})+} \exp\left(-\mathrm{i}\hat{\hat{L}}_S t\right) S_p^{1(\mathrm{L})} \rho_S^{\mathrm{eq}}\right\} \exp(-\mathrm{i}\omega_I t)\mathrm{d}t. \tag{15}$$

The factorization of the correlation function for the composite lattice into two parts leads to a manageable formulation of the spectral density $K_{IS}^{\mathrm{DD}}(-\omega_I)$. Nevertheless, to do this one must be sure that the correlation function $C(t)$ is fully determined by motional processes not related to any degrees of freedom of the S spin included in the Liouville operator $\hat{\hat{L}}_S$. In this equation we have separated also the equilibrium density operator ρ_L^{eq} into the spin part, ρ_S^{eq}, and the part corresponding to the classical degrees of freedom encoded into the correlation function $C(t)$ (one can denote it as ρ_C^{eq}, that $\rho_L^{\mathrm{eq}} = \rho_C^{\mathrm{eq}} \otimes \rho_S^{\mathrm{eq}}$). Since the ρ_C^{eq} quantity represents classical degrees of freedom and therefore $\rho_C^{\mathrm{eq}} = 1$, it is not present explicitly in Eq. (15).

In solid state, crystal systems the orientation of the $\boldsymbol{r}_{IS}$ vector as well as its length can change in time due to jump diffusion of the ions carrying spins I and S between available crystallographic positions. In the particular case, if spins S are fixed on their crystallographic positions, the correlation function $C(t)$ is mediated only by the jump diffusion of the dipolar spins I and one can obviously separate the two correlation functions. If spins S jump between equivalent sites in the crystal lattice, we are allowed to factorize the lattice correlation function as well.

It is so due to the fact that spins S sense always the same local field (for example the same electric field gradient) and, in consequence, their relaxation dynamics is independent of the position which they actually occupy. However, if spins S exhibit exchange dynamics between non-equivalent crystallographic positions, which modulates directly the $I-S$ dipole–dipole coupling and leads at the same time to their relaxation by modulating the second-order interactions, the factorization of Eq. (15) may not be performed any more. Depending on both the nature of the stochastic processes modulating the $I-S$ dipole–dipole interaction and the applied motional model the correlation function $C(t)$ has different mathematical forms. In particular, if the orientation of the dipole–dipole interaction with respect to the laboratory frame is modeled as an isotropic rotational diffusion, the correlation function $C(t)$ results from the expression [3, 25]:

$$\left\langle \frac{D_{m,k}^{l^*}(\Omega_{IS}^{\mathrm{L}}(t))}{r_{IS}^3(t)} \frac{D_{m',k'}^{l'}(\Omega(0))}{r_{IS}^3(0)} \right\rangle = \frac{1}{2l+1} \frac{1}{r_{IS}^6} \delta_{ll'} \delta_{mm'} \delta_{kk'} \exp\left(-\frac{t}{\tau_R^l}\right), \quad (16)$$

while for the exchange motion between crystal sites, as a first attempt, one can use the formula [3, 23, 26]:

$$\left\langle \frac{D_{m,k}^{l^*}\left(\Omega_{IS}^{\mathrm{L}}(t)\right)}{r_{IS}^3} \frac{D_{m',k'}^{l'}\left(\Omega_{IS}^{\mathrm{L}}(0)\right)}{r_{IS}^3} \right\rangle =$$

$$\frac{D_{m,k}^{l^*}\left(\Omega_{IS}^{\mathrm{L}}\right)}{r_{IS}^3} \frac{D_{m',k'}^{l'}\left(\Omega_{IS}^{\mathrm{L}}\right)}{r_{IS}^3} \exp\left(-\frac{t}{\tau_{IS}}\right). \quad (17)$$

In fact, the problem of an appropriate formulation of the correlation function for the jump diffusion is a very complicated issue by itself. The exponential form of the correlation function leads to a straightforward mathematical treatment of the spectral density, $K_{IS}^{\mathrm{DD}}(-\omega_I)$, however one should be aware that it can turn out to be an oversimplification. In fact, the inter-spin distance r_{IS} changes in time due to the exchange motion, but on the other hand one cannot treat this process as a small step translation diffusion. A quite favorable situation takes place for translation diffusion in liquids, which in fact can be modeled as a small step process and described by the correlation function [11, 24, 27]:

$$\left\langle \frac{D_{m,k}^{2^*}\left(\Omega_{IS}^{\mathrm{L}}(t)\right)}{r_{IS}^3(t)} \frac{D_{m',k'}^{2}\left(\Omega(0)\right)}{r_{IS}^3(0)} \right\rangle =$$

$$\delta_{mm'} \delta_{kk'} \frac{72}{5} \frac{N_S}{d^3} \int_0^\infty \frac{u^2}{81 + 9u^2 - 2u^4 + u^6} \exp\left(-\frac{D_{\mathrm{rel}}}{d^2} u^2 t\right) \mathrm{d}u, \quad (18)$$

where D_{rel} is the relative translational diffusion coefficient, defined as a sum of the diffusion coefficients of the molecules carrying spins I and S, d is the distance of the closest approach for the molecules and N_S is the number of spins S per unit volume.

Let us consider as an example the case when the $I-S$ dipole–dipole interaction is modulated by an isotropic molecular tumbling. The single-exponential cor-

relation function of Eq. (16) simplifies appreciably the spectral density $K_{IS}^{\mathrm{DD}}(-\omega_I)$, which takes the form [11, 15]:

$$K_{IS}^{\mathrm{DD}}(-\omega_I) = 6 \left(\frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi r_{IS}^3} \right)^2 \sum_q \begin{pmatrix} 2 & 1 & 1 \\ 1-q & q & -1 \end{pmatrix}^2$$

$$\times \int_0^\infty \mathrm{Tr}_S \left\{ S_q^{1(\mathrm{L})+} \exp \left(-\mathrm{i}\hat{\hat{L}}_S t \right) S_q^{1(\mathrm{L})} \rho_S^{\mathrm{eq}} \right\} \exp \left[-\left(\mathrm{i}\omega_I + \frac{1}{\tau_R} \right) \right] \mathrm{d}t =$$

$$\frac{1}{10} \left(\frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi r_{IS}^3} \right)^3 [s_{11}(-\omega_I) + 3s_{00}(-\omega_I) + 6s_{-1-1}(-\omega_I)]. \tag{19}$$

The S spin Liouville operator, $\hat{\hat{L}}_S$, can be expressed as a sum of the Liouvilian $\hat{\hat{L}}_S^0$ representing the static interaction and the relaxation superoperator $\hat{\hat{R}}_S$ obtained in the way described in the previous section. So far we have not commented very much on the consequences of expressing the tensor operators S_q^1 in the laboratory frame. We have started the considerations from the laboratory representation of the dipole–dipole Hamiltonian of Eq. (12). Therefore the operators $S_q^{1(\mathrm{L})}$ appear "automatically" in the formulation of the spectral density of Eq. (14) and until now we did nothing on them, because the calculations are complicated enough anyway. However, it implies that we have assumed implicitly that the Zeeman coupling provides the main interaction for the S spin, i.e. it is quantized in the laboratory frame. Independently of the timescales of motional processes occurring in the system under interest, if the Zeeman interaction dominates over the second--order interactions it determines the energy level structure of the S spin. Thus, the spectral density given by Eq. (19) describes the I spin relaxation in the high field regime. One can write Eq. (19) in a form much more suitable for the computation by introducing the superoperator $\hat{\hat{M}}$ including the S spin operators, $\mathrm{i}\hat{\hat{L}}_Z(S) + \hat{\hat{R}}_S$, and the term $\mathrm{i}\omega_I + \tau_R^{-1}$ [8, 9, 11–15, 20–24]:

$$\hat{\hat{M}} = \mathrm{i}\hat{\hat{L}}_Z(S) + \hat{\hat{R}}_S + \left(\mathrm{i}\omega_I + \tau_R^{-1} \right) \hat{\hat{1}}, \tag{20}$$

where $\hat{\hat{1}}$ is the unit superoperator. Consequently the spectral densities may be expressed as [15]:

$$s_{qq}(-\omega_I) = \frac{1}{2S+1} \int_0^\infty \mathrm{Tr}_S \left[S_q^{1(\mathrm{L})+} \exp \left(-\hat{\hat{M}}t \right) S_q^{1(\mathrm{L})} \right] \mathrm{d}t. \tag{21}$$

The factor $1/(2S+1)$ comes from the equilibrium density operator, ρ_S^{eq}, under high temperature approximation. The operator $\hat{\hat{M}}$ as well as the tensor components, S_q^1, may be represented as matrices ($\left[\hat{\hat{M}} \right]$ and $\left[S_q^1 \right]$, respectively) in the Liouville basis $\{ |m_S^\alpha\rangle\langle m_S^\beta| \} \equiv |m_S^\alpha, m_S^\beta\rangle$ constructed from the Zeeman eigenstates of spin S. The matrix elements of the operator $\hat{\hat{M}}$ are given as

$$\left[\hat{\hat{M}}\right]_{\alpha'\beta'\alpha\beta} = \left(m_S^{\alpha'}, m_S^{\beta'}|\hat{\hat{M}}|m_S^{\alpha}, m_S^{\beta}\right) =$$

$$\left(\mathrm{i}\omega_{\alpha\beta} + \mathrm{i}\omega_I + \tau_R^{-1}\right)\delta_{\alpha'\alpha}\delta_{\beta'\beta} + R_{\alpha\alpha'\beta\beta'}|_{\omega_{\alpha\beta}=\omega_{\alpha'\beta'}}, \tag{22}$$

where the mark $\Big|_{\omega_{\alpha\alpha'}=\omega_{\beta\beta'}}$ refers to the secular approximation; it indicates that only the relaxation matrix elements $R_{\alpha\alpha'\beta\beta'}$ which connect the coherences with $\omega_{\alpha\beta} = \omega_{\alpha'\beta'}$ are relevant. The matrices (vectors) $\left[S_q^{1(\mathrm{L})}\right]$ are determined by the relations [4]:

$$S_0^1 = S_z = \sum_{m_S=-S}^{S} m_S|m_S\rangle\langle m_S|, \tag{23a}$$

$$S_1^1 = -\frac{1}{\sqrt{2}}S_+ = -\frac{1}{\sqrt{2}}\sum_{m_S=-S}^{S-1}\sqrt{(S-m_S)(S+m_S+1)}|m_S+1\rangle\langle m_S|, \tag{23b}$$

$$S_{-1}^1 = \frac{1}{\sqrt{2}}S_- = \frac{1}{\sqrt{2}}\sum_{m_S=-S+1}^{S}\sqrt{(S+m_S)(S-m_S+1)}|m_S-1\rangle\langle m_S|. \tag{23c}$$

Explicit forms of the spectral densities, $s_{qq}(-\omega_I)$, can be obtained as a product of the corresponding matrices

$$s_{qq}(-\omega_I) = \frac{1}{2S+1}\left[S_q^{1(\mathrm{L})}\right]^+\left[\hat{\hat{M}}\right]^{-1}\left[S_q^{1(\mathrm{L})}\right]. \tag{24}$$

It is of some interest to consider the I spin relaxation at low field limit when the S spin is placed in a highly asymmetric environment, so that the static components of the second-order interactions dominate over their transient counterparts [11–15, 23, 24]. At the low field limit the principal axis systems for the I and S spins are different. The first one is locked in the laboratory frame, while the second one in the principal system of the ZFS or the quadrupole tensor. Since we have actually decomposed the $I-S$ dipole–dipole Hamiltonian in the I and the S spin tensor operators, we can represent the operators $S_q^{1(\mathrm{L})}$ in the molecular frame (M) by applying the transformation rule: $S_q^{1(\mathrm{L})} = \sum_{m=-1}^{1} S_m^{1(\mathrm{M})}D_{mq}^1\left(\Omega_{\mathrm{M}}^{\mathrm{L}}\right)$. It implies that the correlation function $C(t)$ takes in the low field the form [13, 23, 24]:

$$C(t) =$$

$$\left\langle \frac{D_{0,1-q}^{2*}\left(\Omega_{IS}^{\mathrm{L}}(t)\right)D_{m,q}^{1*}\left(\Omega_{\mathrm{M}}^{\mathrm{L}}(t)\right)}{r_{IS}^3(t)}\frac{D_{0,1-p}^{2}\left(\Omega_{IS}^{\mathrm{L}}(0)\right)D_{m,p}^{1}\left(\Omega_{\mathrm{M}}^{\mathrm{L}}(0)\right)}{r_{IS}^3(0)}\right\rangle. \tag{25}$$

If the molecular frame coincides with the $I-S$ dipole–dipole axis, $\Omega_{IS}^{\mathrm{L}} = \Omega_{\mathrm{M}}^{\mathrm{L}}$, the expression can be appreciably simplified by contracting the Wigner rotation matrix elements according to elementary angular momentum theory [4]:

$$D_{0,1-q}^2 D_{mq}^1 =$$

$$(-1)^{m+1} \sum_\lambda (2\lambda + 1) \begin{pmatrix} 2 & 1 & \lambda \\ 0 & m & -m \end{pmatrix} \begin{pmatrix} 2 & 1 & \lambda \\ 1-q & q & -1 \end{pmatrix} D_{m,1}^\lambda. \qquad (26)$$

Properties of the 3-j symbols restrict the summation to the terms of $\lambda = 1$. As a result the dipolar spectral density becomes [11–13, 15]:

$$K_{1,1}^{\mathrm{DD}}(-\omega_I) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{r_{IS}^3} \right)^2 \left[s_{11}^{\mathrm{LF}}(-\omega_I) + 4 s_{00}^{\mathrm{LF}}(-\omega_I) + s_{-1-1}^{\mathrm{LF}}(-\omega_I) \right], (27)$$

where the low field (LF) spectral densities, $s_{qq}^{\mathrm{LF}}(-\omega_I)$, can be evaluated in the already described manner as

$$s_{qq}^{\mathrm{LF}}(-\omega_I) = \int_0^\infty \mathrm{Tr}_S \left\{ S_q^{1(\mathrm{M})*} \exp\left[-\left(\mathrm{i}\hat{\hat{L}}_{\mathrm{ZFS}(Q)}^0(S) + \hat{\hat{R}}_S \right) t \right] S_q^{1(\mathrm{M})} \right\}$$

$$\times \exp\left(-\mathrm{i}\omega_I t + \frac{t}{3\tau_R} \right) \mathrm{d}t = \left[S_q^{1(\mathrm{M})} \right]^+ \left[\hat{\hat{M}}_{\mathrm{LF}} \right]^{-1} \left[S_q^{1(\mathrm{M})} \right]. \qquad (28)$$

The operator $\hat{\hat{M}}_{\mathrm{LF}}$ is defined as $\hat{\hat{M}}_{\mathrm{LF}} = \mathrm{i}\hat{\hat{L}}_{\mathrm{ZFS}(Q)}^0(S) + \hat{\hat{R}}_S + \left(\frac{1}{3\tau_R} + \mathrm{i}\omega_I \right) \hat{\hat{1}}$. It includes in full analogy to the high field operator $\hat{\hat{M}}$ the main interaction for the S spin, the appropriate relaxation superoperator $\hat{\hat{R}}_S$, the rotational exponential decay (characterized now by the correlation time associated with the first-order Wigner matrices) and the nuclear spin transition frequency ω_I.

6. Validity regimes of the perturbation description of the dipolar and quadrupole (electron) spin dynamics

In this section we aim for a detailed and careful discussion of validity regimes of the perturbation treatment applied to the S and the I spin systems, depending on the motional conditions and relative strengths of the spin interactions. In this paper we have presented in more detail some examples of spin systems for the purpose of illustrating the main concept of the composite lattice and the computational formalism. For instance, we have dealt with the field dependent S spin relaxation under the condition that the orientation of the principal axis system of the static interactions (the ZFS or the quadrupole coupling) relative to the laboratory frame does not change in time. We have presented the idea of treating the S spin subsystem as a part of the lattice for the I spin in two limiting magnetic field regimes (at high and low magnetic fields). The examples have been chosen with the intention of providing a theoretical background, which can be adapted in a straightforward way to various spin systems and different motional conditions, if the requirements of the second-order perturbation theory are fulfilled. Therefore, clear mathematical formulations of the validity regimes of this quite general description and some comments how motional conditions

combined with strengths of relevant interactions alter the computations are highly appropriate.

We begin the discussion from spins systems for which the orientation of the molecular frame with respect to the laboratory axis is fixed. Therefore, the energy level structure of the S spin can be described, for an arbitrary magnetic field, by a superposition of the Zeeman coupling and the averaged part of the corresponding second-order interaction. The relaxation mechanism is provided, independently of the applied magnetic field, by the transient ZFS or the transient part of the quadrupole interaction. Validity criteria of the relaxation theory applied to the S spin subsystem have been formulated in Sect. 4. For completeness of the present discussion we repeat them at this stage; it is required that $\left|H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_{\mathrm{D}}\right| \ll 1$ and $\left|H_{\mathrm{ZFS}}^{\mathrm{S}}/H_{\mathrm{ZFS}}^{\mathrm{T}}\right| \gg \left|H_{\mathrm{ZFS}}^{\mathrm{T}}\tau_V\right|$ or $\left|H_Q^{\mathrm{T}}\tau_Q\right| \ll 1$ and $\left|H_Q^0/H_Q^{\mathrm{T}}\right| \gg \left|H_Q^{\mathrm{T}}\tau_Q\right|$ for the electron and the quadrupole spin, respectively. The conditions can be fulfilled by, for example, slowly rotating molecular systems (like large complexes of transition metal ions interacting with the surrounding water molecules) or crystal solid state systems with spins S fixed on their positions in the lattice [11, 12, 14, 23]. We have not discussed the I spin relaxation for this case. However, we have pointed out that it is essential for explicit evaluations of the spectral density $K_{IS}^{\mathrm{DD}}(-\omega_I)$ to decompose the motion modulating the Ω_{ML} angle from the S spin dynamics and the decomposition is straightforward for this class of systems. In fact, in this case one deals with the orientation-specific relaxation of the I spin, because the orientation of the molecular frame remains unchanged in time. Even though the S spin fulfills the requirements of the perturbation theory, it does not imply that the theory is applicable to the I spin. Generally, the $I-S$ dipole–dipole coupling is modulated by various motional processes, like rotational and translational diffusion, exchange motion, some other kinds of jump dynamics, and the S spin relaxation. We treat the processes as uncorrelated, which implies that they contribute independently to the effective stochastic fluctuations of the mutual $I-S$ coupling. Therefore one can think about a set of correlation decay constants, $\tau_{\mathrm{c},i}^{-1}$, describing the particular motional processes in terms of a superposition of their characteristic time constants, for example $\tau_{\mathrm{c},i}^{-1} = \tau_{\mathrm{M}}^{-1} + R_{(Q),i}$, where τ_{M} reflects some exchange dynamics of the I and (or) S spins, while $R_{(Q),i}$ describes individual quadrupole spin relaxation rates. For the presently discussed case the S spin relaxation becomes in fact the only one, effective source of the modulation of the dipole–dipole interaction. Therefore one must consider with caution whether the S spin relaxation is efficient enough to fulfill the Redfield condition for the I spin $|H_{\mathrm{DD}}(I,S)\tau_{\mathrm{c}}| \ll 1$. One should be aware that the S spin exhibits a complex multiexponential relaxation depending on the magnetic field and strongly affected (particularly in the low field) by the static second-order interactions. This problem is particularly important for systems containing slowly relaxing quadrupole spins [23]; the electron spin relaxation is usually very fast.

This treatment can be extended to a certain degree to systems with faster modulations of the Ω_{ML} angle. One can deal with motion fast enough to have a non-negligible effect on the dipole–dipole interaction, but still much slower than the S spin relaxation. In this motional regime the S spin possesses the same energy level structure resulting from the Zeeman coupling and the static ZFS (the static quadrupole coupling), which from the point of view of the S spin still do not change in time their relative orientation. The motion modulating the orientation of the molecular frame and the spin relaxation can be still treated as uncorrelated, because of timescale separation, and the corresponding correlation functions can be separated. This motional regime has been discussed in the context of electron spin relaxation and rotational modulations of the $I-S$ dipole–dipole interaction in [28] and called the "moderatory slow rotation". The treatment breaks down starting from the high field limit since the S spin relaxation is here slower than at low field and therefore more close to the timescale of the motion responsible for the momentary orientation of the molecular and the laboratory frames. If this motion becomes faster the perturbation approach is not longer valid for the quadrupole (electron) spin. One cannot separate the correlation function related to the modulations of the Ω_{ML} angle from the S spin dynamics, because both the processes occur on a similar timescale. From the perspective of the S spin one is not able to establish the role of the static components of the ZFS or the quadrupole coupling, respectively. One may not include it into the main Hamiltonian, because its superposition with the Zeeman coupling does not lead to a well-defined, time-independent energy level structure any more. One may not treat it as the relaxation mechanism, either, because the motion is not fast enough to fulfill the Redfield condition. Thus, the decomposition breaks down at the same time as the means that the Redfield equation of motion is no longer valid for the electron spin. It implies of course that the relaxation of the I spin cannot be described in a manner which requires an explicit and clear definition of the S spin relaxation rates. In fact, the low field limit is an exception. Since the Zeeman coupling is negligible, the static second-order interactions act as the main Hamiltonian for the quadrupole (electron) spin, if it dominates over the transient counterpart [15, 24], independently of the timescale of the motion modulating the orientation of the molecular frame. Thus, the validity conditions of low field description of the I spin relaxation presented in the previous section are related to the transient parts of the second-order couplings: it is required that the amplitude of the static interaction is larger than that of the transient one, and the transient ZFS (quadrupole) Hamiltonian fulfills the Redfield condition: $\left| H_{(2)}^{\mathrm{T}} \tau_{\mathrm{D}(V)} \right| \ll 1$. If, because of high symmetry of the molecular environment, there is no static ZFS (no static quadrupole coupling), the decomposition problem does not exist at all: the $I-S$ dipole–dipole axis changes its orientation due to, for example, molecular tumbling, while the electron (quadrupole) spin relaxation is caused by a different motional process (for example lattice vibrations) affecting the corresponding

transient interaction. Finally, we approach the motional limit when the static interactions are modulated fast enough, so that they fulfill the Redfield condition: for example $\left| H_{(2)}^{\mathrm{S}} \tau_{\mathrm{R}} \right| \ll 1$. Now, the role of the static interactions is well defined, at least in the high field limit. They provide a relaxation mechanism for the quadrupole (electron) spin, which can be included into the relaxation operator $\hat{\hat{R}}_S$ of Eq. (20). Nevertheless, in the intermediate range of the magnetic field, if the Zeeman and the static second-order interactions are comparable, it is impossible to decompose the total Hamiltonian into a main and a perturbing part, so that one cannot define the S spin relaxation.
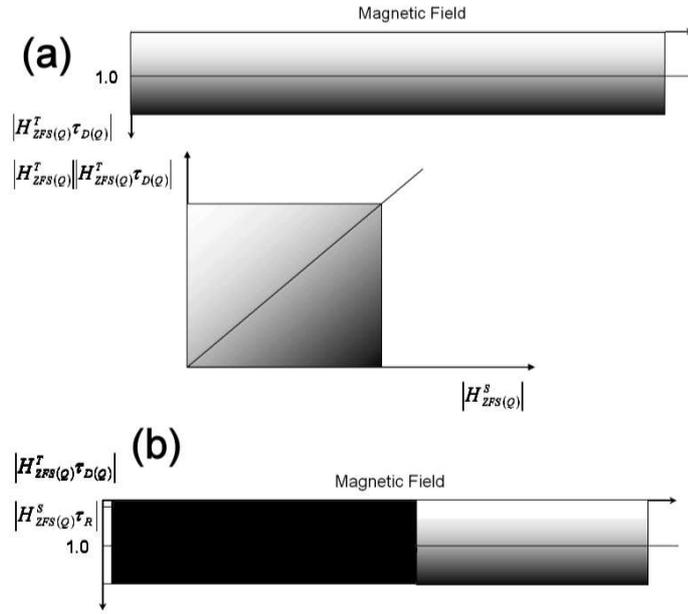

Fig. 4.   Validity regimes of the perturbation description of the S spin system characterized by a large static ZFS (quadrupole) tensor: the relative orientation of the molecular and laboratory frames is fixed (a), the molecular frame fluctuates very fast relative to the laboratory one (b).

The validity regimes of the presented description of field dependent relaxation processes are illustrated in Fig. 4a, b. White areas represent the regimes where the perturbation treatments are applied. Their applicability becomes problematic under the conditions represented by gray areas and finally the perturbation approaches break down (black areas).

7. Concluding remarks

We have presented a review of recent theoretical models describing field dependent relaxation processes in complex systems containing mutually coupled

dipolar, quadrupole, and electron spins. Analogies between quadrupole and electron spin systems have been pointed out. We have discussed in detail validity conditions of the presented models, based on the second-order perturbation theory.

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