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Evolution of solid state systems containing mutually coupled dipolar and quadrupole spins: Perturbation treatment

Danuta Kruk[a,b,*], Oliver Lips[a]

[a]Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany
[b]Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

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Abstract

Perturbation approach to time evolution of multi-spin systems containing quadrupole and dipolar spins has been presented and discussed. The treatment comprises polarization transfer effects, field-dependent relaxation processes of dipolar as well as quadrupole spins and combined results of both of them. Complete theories dealing with various aspects of the spin dynamic processes have been proposed. Because of an educational character of this paper, relevant assumptions, limitations and even particular steps of the proposed treatments have been discussed in detail. Special emphasis is put on understanding of validity regimes of the perturbation treatment, depending on relative strengths of spin interactions and timescales of relevant motional processes affecting them. Motional regimes required for spins to be involved in essentially different evolution pathways like polarization transfers or relaxation have been illustrated by experimental examples.

Keywords: Quadrupole interactions; Polarization transfer; Dipolar relaxation; Quadrupole relaxation; Coupled spins

1. Introduction

Fast development of field cycling techniques gives possibility to perform experiments in a wide range of magnetic fields for a variety of multi-spin systems. Field-dependent relaxation and polarization transfer studies can be an important source of information on dynamic properties of such systems, provided that an adequate theoretical model is available. To supply reasonable theoretical tools for modeling and interpreting field dependencies of observables reflecting the spin interactions and dynamics is, in this context, of primary importance.

Dynamics of an arbitrary spin system is governed by the Liouville von Neumann equation [1–6], describing time evolution of its density operator under Hamiltonian covering all relevant interactions. A common way to solve this equation is based on the perturbation approach, which leads in particular to the Redfield relaxation theory [1–6]. Depending on the relative strengths of specific interactions included into the Hamiltonian and on motional conditions, the interactions can act as a principal origin of the energy level structure of the spin system, as a source of spin relaxation or as both. A strong interaction in combination with relatively slow motion can bring the spin dynamics outside the validity conditions of the Redfield relaxation theory.

Motivated by several misunderstandings of some aspects of the spin evolution, by treatments neglecting some really pertinent effects without any justification (like for example the fact that quadrupole or electron spins can exhibit a complicated energy level structure and their own relaxation pathways), or by approaches based on the perturbation theory, even if motional conditions of the considered systems do not allow for this type of description, we decided to discuss in detail some exemplifying cases of spin evolution in the context of the validity conditions of the perturbation theory.

In this paper we deal with spin systems containing dipolar and quadrupole spins mutually coupled by dipole–dipole interactions. Such systems are very attractive

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*Corresponding author. Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany. Fax: +49 6151 162833.
E-mail address: danuta.kruk@physik.tu-darmstadt.de (D. Kruk).

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because of a variety of effects caused by interplay and competition between degrees of freedom of the quadrupole and dipolar spins, and carrying in this way unique information about structure and dynamics. However, the systems are also very demanding from the point of view of a proper theoretical treatment, being actually the only way to understand really their evolution and profit from experimental abilities.

The paper is organized as follows: Section 2 summarizes essential elements of the Liouville von Neumann formulation for the convenience of readers. Validity regimes of the perturbation treatment are specially emphasized. Section 3 covers theories of some relevant pathways of the complex evolution of multi-spin systems. The theoretical treatment includes:

- Polarization transfer effects.
- Polarization transfer effects affected by fast dynamics of neighboring dipolar spins not coupled directly to the quadrupole ones.
- Field-dependent relaxation processes of dipolar as well as quadrupole spins.
- Simultaneous effects of polarization transfer and relaxation processes.

The considered problems are illustrated by experimental examples. The last section contains concluding remarks.

2. Fundamentals

Most of the essential elements of the theoretical framework used in this paper are based on the Liouville von Neumann equation [1–6] describing time evolution of an arbitrary spin system, employing the density matrix formalism [1–5,7,8]. This section is devoted to the theoretical tools appropriate to a subsequent treatment of mutually interacting spin systems, which exhibit various motional degrees of freedom. Depending on the strengths of the particular spin interactions and the motional conditions, one can consider various aspects of spin dynamics, particularly spin relaxation. The essence of the relaxation theory is the series of physically based approximations, which are invoked in order to obtain the Redfield equation of motion [1–5,9–12]. Here we present an overview of the perturbation approach to the Liouville von Neumann equation together with some important comments concerning validity regimes of this treatment. We do not go beyond textbook considerations. We only summarize what is necessary for the clarity of this paper.

2.1. Liouville von Neumann equation and the perturbation approach

Time evolution of a density operator $\rho(t)$ for a spin system described by a Hamiltonian H is governed by the Liouville von Neumann equation:

$$\frac{d}{dt}\rho(t) = -i[H, \rho(t)]. \tag{1}$$

Solution of this differential equation may be obtained by perturbation treatment. The perturbation approach requires that the total Hamiltonian H can be divided into a main part H_0 which determines energy level structure for the considered system, and a small perturbing term H_R describing a coupling between the spin system and a lattice and causing transitions between the energy levels. The transformation to the interaction representation [1–6], generated by the main Hamiltonian H_0: $\rho'(t) = \exp(-iH_0t)\rho(t)\exp(iH_0t)$ and $H'_R(t) = \exp(-iH_0t)H_R\exp(iH_0t)$, simplifies the equation to the form:

$$\frac{d}{dt}\rho'(t) = -i[H'_R(t), \rho'(t)]. \tag{2}$$

The perturbation approach to this differential equation is to rewrite it in integration form and then substitute it into itself iteratively, involving a set of conditions. The assumption that the second order perturbation theory describes the system well (i.e. the higher order terms in this expansion are negligible) is called 'the Redfield limit' and is the fundamental assumption of the Redfield relaxation theory [1–5,9–12]. It brings us to the concept of the correlation time τ_c characterizing the perturbing interaction. The memory between $H'_R(t)$ and $H'_R(t-\tau)$ only lasts for a short time, where τ_c describes the timescale of stochastic fluctuations of the spin–lattice coupling. Invoking the correlation time, one can establish an exact mathematical formulation for the Redfield limit, called also the motional narrowing condition or the strong narrowing condition, as: $|H_R|\tau_c \ll 1$where $|H_R|$ is expressed in angular frequency units, [1–6,9–12]. Under this condition the Liouville equation can be transformed to a set of coupled equations for particular matrix elements of the density operator, $\rho'_{\alpha\alpha'}(t)$, by taking its matrix representation in the basis constructed from the eigenstates $|\alpha\rangle$ of the main Hamiltonian H_0:

$$\frac{\rho'_{\alpha'}(t)}{dt} = \sum_{\beta\beta'} \Gamma_{\alpha\alpha'\beta\beta'} \exp[i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})]\rho'_{\beta}(t). \tag{3a}$$

The frequencies $\omega_{\alpha\alpha'}$ are the transition frequencies between the eigenstates $|\alpha\rangle$ and $|\alpha'\rangle$ of the system: $\omega_{\alpha\alpha'} = \omega_\alpha - \omega_{\alpha'}$. To obtain a system of differential equations with constant (time-independent) coefficients $\Gamma_{\alpha\alpha'\beta\beta'}$ coupling the time evolution of the element $\rho_{\alpha\alpha'}(t)$ to the elements $\rho_{\beta\beta'}(t)$ all the expressions $\omega_{\alpha\alpha'} - \omega_{\beta\beta'}$, unless equal zero, must be large compared to the rate of change of the density matrix, represented by the coefficient $\Gamma_{\alpha\alpha'\beta\beta'}$. One can formulate this condition in an equivalent manner, saying that the Hamiltonian H_0 must provide a stationary basis set for the considered spin, so the timescale of the oscillations must be much faster than the spin relaxation timescale. It means that the Hamiltonian H_0 chosen as the main interaction and therefore determining the