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journal homepage: www.elsevier.com/locate/ssnmrLocal-field approximation of homonuclear dipolar interactions in ${}^7\text{Li}$ -NMR: Density-matrix calculations and random-walk simulations tested by echo experiments on borate glassesMichael Storek^{a,*}, Kenneth R. Jeffrey^b, Roland Böhmer^a^a Fakultät Physik, Technische Universität Dortmund, 44221 Dortmund, Germany^b Department of Physics, Guelph-Waterloo Physics Institute, University of Guelph, MacNaughton Building, Gordon Street, Guelph, Ontario, Canada N1G 2W1

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ABSTRACT

NMR echo techniques have proven to be important to study dynamics in ion conductors and other solid materials. Using the spin-3/2 nucleus ${}^7\text{Li}$ as a probe, both the quadrupolar and the often neglected homonuclear dipolar interactions modulate the NMR frequency as the ion performs jump processes. Retaining only the local-field term of the many-body Hamiltonian, the impact of the dipolar interaction on various echo experiments was studied using spin dynamics calculations yielding products of dipolar and quadrupolar correlation functions. Using a simple stochastic model these functions were simulated with particular emphasis on the impact of ionic motions and on the conditions under which the dipolar and quadrupolar contributions factorize. The results of the computations and of the random-walk simulations are compared with experimental data obtained for various lithium borate and lithium borophosphate glasses. It is concluded that the local-field approximation is a useful means of treating the Li–Li dipole interactions and that the simple model that we introduce is capable of describing many experimentally observed features. Furthermore, because the dipolar and quadrupolar contributions essentially factorize, a selective determination of the corresponding correlation functions becomes possible.

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1. Introduction

In recent years there has been much interest in developing and optimizing Li ion conductors and there still is a major effort directed at achieving further technological progress in maximizing the conductivity. To monitor the charge transport dynamics in amorphous and crystalline Li electrolytes a host of experimental and theoretical techniques are used [1]. When paving the way to improved material performance, it is important to understand in detail the factors that govern the conductivity in modern solid electrolytes, see, e.g., Ref. [2]. One of the fundamental questions in this context is whether the motion of the ions can be described in an effective single-particle picture or whether the interaction and correlation effects among the charged mobile species have to be taken into account from the outset [3–6].

Among other methods, various nuclear magnetic resonance (NMR) relaxation and echo techniques have been extensively exploited to probe ion dynamics on a local scale. The quadrupolar, the dipolar, and other interactions can modulate the NMR frequency

as an ion performs various jump processes. Thus, by tracking the evolution of the NMR frequency of such nuclear probes as ${}^6\text{Li}$ or ${}^7\text{Li}$, it is possible to gain information about the ionic motion. The NMR frequency of these probes predominantly reflects the coupling of the Li nuclear electrical quadrupole moment to the distribution of charges in their environment. To the extent to which this so called quadrupolar frequency ω_Q reflects solely the properties of a single mobile ion, a relatively straightforward single-particle treatment in the derivation of the associated NMR correlation functions is allowed.

This situation changes when contributions to the NMR frequency are to be taken into account which depend on the coupling of the probe nucleus to other mobile ions. Here, the nuclear dipole–dipole interactions, in particular those among the ${}^7\text{Li}$ nuclei which exhibit a large nuclear dipole moment (expressed in terms of the gyromagnetic ratio γ), come to mind. Nevertheless, since the dipolar contributions to the hopping induced modulation of the overall NMR frequency are typically at least one order of magnitude smaller than the quadrupolar one, many previous investigations focused solely on the quadrupolar interaction [7–10].

Furthermore, an exhaustive treatment of the dipolar interactions is demanding for at least two reasons: On the one hand, the many-bodied nature of the nuclear dipole–dipole interaction is

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complex and therefore various approximations have been suggested and tested in the past. One of these approaches, which we will dwell upon in the present work, just considers the local dipolar field that the environmental nuclei generate at the probe site [11]. This simplification has turned out to be most useful in the context of the NMR of ${}^6\text{Li}$ with its relatively small gyromagnetic ratio γ_6 (where $\gamma_6/\gamma_7 \approx 0.379$). However, the results obtained for the spin $I=1$ nucleus ${}^6\text{Li}$ cannot be applied directly to the other isotope since ${}^7\text{Li}$ has a different spin, $I=3/2$. This circumstance requires the explicit calculation of the spin dynamics for ${}^7\text{Li}$ that will be outlined in Section 2.

Even more challenging, on the other hand, is the many-body aspect of the dipolar interaction and the resulting phenomena. In general, this situation cannot be treated analytically although results may be accessible, e.g., via molecular dynamics simulations [12]. To grasp some of the basic features and consequences of the multi-particle character of the transport processes in question, in Section 3 we introduce a simple stochastic model of ionic hopping on a spherical shell from which motional correlation functions (CFs) can profitably be computed via random-walk simulations. The simple model that we have developed allows us to compare the dipolar multiple-particle CFs with the quadrupolar single-particle CFs. Anticipating that in general the spin dynamics calculations in Section 2.3 yield products of dipolar and quadrupolar CFs, it is also important to explore whether and to which extent these two contributions can be separated. If a factorization can be achieved it should be possible to obtain separate dipolar and quadrupolar CFs.

To test many of the theoretical considerations we have performed ${}^7\text{Li}$ NMR echo experiments on glasses containing either mobile or essentially immobile Li ions. Furthermore, the strength of the homonuclear dipole interactions was varied experimentally by using samples with ${}^6\text{Li}:$ ${}^7\text{Li}$ ratios either equal to 7.4:92.6 (natural abundances) or 95:5 (isotopically enriched).

2. Density matrix calculations

For ${}^7\text{Li}$ with $I=3/2$ the secular part of the first-order quadrupolar Hamiltonian for a spin α is given by

$$H_Q^{(\alpha)} = \frac{1}{6}\omega_Q^{(\alpha)}[3I_Z^{(\alpha)}I_Z^{(\alpha)} - I(I+1)]. \quad (1a)$$

Here

$$\omega_Q = \frac{1}{2}\delta_Q(3\cos^2\theta_Q - 1 - \eta_Q \sin^2\theta_Q \cos 2\phi_Q) \quad (1b)$$

and δ_Q and η_Q denote the anisotropy and the asymmetry parameter, respectively. The angles θ_Q and ϕ_Q determine the orientation of the electric field gradient (EFG) tensor at a specific spin site in the usual fashion. Typically, the quadrupolar splitting is about $\delta_Q \approx 2\pi \times 100$ kHz or less, thus second-order effects can safely be neglected. The resulting NMR spectrum consists of quadrupolarly perturbed satellite transitions, i.e., $m = +3/2 \leftrightarrow m = +1/2$ and $m = -1/2 \leftrightarrow m = -3/2$, with m denoting the magnetic quantum number, and a non-perturbed central transition, $m = -1/2 \leftrightarrow m = +1/2$.

Although the quadrupolar interaction dominates the spin evolution in the rotating frame, dipolar contributions, giving rise to an additional broadening of the NMR spectrum, cannot in general be neglected. In particular, a significant broadening of the central line provides an estimate of the magnitude of the dipolar interaction. For ${}^7\text{Li}$ the dipolar line width, full width at half maximum (FWHM), is typically about $\Delta\nu_D \approx 2\pi \times 5$ kHz and, thus, only about one order of magnitude smaller than the quadrupolar interaction. Discussing the dipolar interactions is rather complicated since flip-flop mechanisms couple the entire spin system and any analysis of the time evolution becomes a many-body

problem [13]. The secular part of the homonuclear dipolar interaction among all N pairs of spins α and β can be written as

$$H_D = - \sum_{\alpha,\beta}^N \hbar \frac{\mu_0 \gamma^2}{4\pi r_{\alpha,\beta}^3} \frac{1}{2} (3 \cos^2 \theta_{\alpha,\beta} - 1) \left[2I_Z^{(\alpha)} I_Z^{(\beta)} - \frac{1}{2} (I_+^{(\alpha)} I_-^{(\beta)} + I_-^{(\alpha)} I_+^{(\beta)}) \right]. \quad (2)$$

Here, $\theta_{\alpha,\beta}$ denotes the angle between the internuclear vector and the external magnetic field, γ is the gyromagnetic ratio of the spins, and $r_{\alpha,\beta}$ is the distance between them. The spin part of Eq. (2) consists of a local-field term $I_Z^{(\alpha)} I_Z^{(\beta)}$ and a flip-flop term described by $(I_+^{(\alpha)} I_-^{(\beta)} + I_-^{(\alpha)} I_+^{(\beta)})$. Qi et al. [14] have provided an analytical description for dipolarly coupled pairs of ${}^7\text{Li}$ -spins systematically evolving under a stronger secular quadrupolar Hamiltonian. When diagonalizing the corresponding Hamilton operator, only elements involving the central transition were retained. This simplification was motivated by the recognition that in a crystal of complex structure or in an amorphous solid, the energy levels of the satellite transitions are expected to be mismatched for adjacent ${}^7\text{Li}$ nuclei thus rendering flip-flop transitions ineffective. Neither the heteronuclear dipole nor the chemical shift interactions were considered in these computations. Calculations of the NMR signal for $I=3/2$ including a local Zeeman term were provided by Tang and Wu [15] for the application of the usually applied Jeener–Broekaert pulse-sequence [16]. However, the authors argued that for ${}^9\text{Be}$ ($I=3/2$) contributions from local-field terms can effectively be suppressed if the spin-labeling evolution time t_p is chosen to be shorter than the inverse dipolar line width, $t_p \ll (\Delta\nu_D)^{-1}$.

In a different approach the flip-flop terms were entirely neglected for $I=1$ systems, e.g., ${}^2\text{H}$ and ${}^6\text{Li}$, which do not exhibit a central line [11]. Under this assumption the multi-spin problem is reduced to a sum of single-spin Hamiltonians

$$H_D = \sum_{\alpha} \omega_D^{(\alpha)} I_Z^{(\alpha)} \quad (3a)$$

with

$$\omega_D^{(\alpha)} = - \sum_{\beta} \hbar \frac{\mu_0 \gamma^2}{4\pi r_{\alpha,\beta}^3} (3 \cos^2 \theta_{\alpha,\beta} - 1) \langle I_Z^{(\beta)} \rangle, \quad (3b)$$

where the brackets $\langle \rangle$ denote the expectation value for the operator. Within this approach, i.e., Eq. (3a), H_D defines a site-specific resonance offset corresponding to the local-field $\omega_D^{(\alpha)}/\gamma$ at the Li ion site. Such a treatment of the dipolar interaction as a local field has been investigated before in the framework of deuterium ($I=1$) [17–19] and ${}^6\text{Li}$ NMR [11]. Here, the effect of the local-field terms of the dipolar interaction was calculated and explicit expressions for the solid echo and for the dephasing of the double-quantum coherence were derived. Considering a stochastic spin evolution it was also shown that the transverse relaxation due to the dipolar interaction in spin $I=1$ systems can be adequately treated.

For ${}^6\text{Li}$ in lithium borate glasses it was ascertained [11] that the quadrupolar and the dipolar interactions are of the same order of magnitude. Nevertheless, it was possible, at least for a lithium borate glass in which ionic motions are effectively frozen, to understand the spin dynamics using a single-spin approximation because the ${}^6\text{Li}$ - ${}^6\text{Li}$ dipolar interaction turned out to be negligible. Its contribution to the total dipolar interaction amounts to less than 1% in a sample with natural abundance (7.4%) of ${}^6\text{Li}$. In these glasses the ${}^6\text{Li}$ - ${}^7\text{Li}$ heteronuclear interactions were found to be approximately 5 times stronger but still the majority of the dipolar coupling stems from the neighboring boron atoms.

For a typical Li–Li distance of $r_{\alpha,\beta} = 3 \text{ \AA}$ the ratio of dipole–dipole to quadrupolar interaction strength ($\propto \gamma^2/Q$) for ${}^7\text{Li}$ is by a factor of about 7.1 times smaller than for ${}^6\text{Li}$. Nevertheless, the large natural ${}^7\text{Li}$ abundance of 92.6% renders the homonuclear dipole–dipole ${}^7\text{Li}$ - ${}^7\text{Li}$ interactions relatively strong [7]. To analyze their

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