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Physica B 366 (2005) 127–137
PHYSICA B
www.elsevier.com/locate/physb

Propagator formalism and computer simulation of restricted diffusion behaviors of inter-molecular multiple-quantum coherences

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Received 31 March 2005; received in revised form 13 May 2005; accepted 18 May 2005

Abstract

In this paper, behaviors of single-quantum coherences and inter-molecular multiple-quantum coherences under restricted diffusion in nuclear magnetic resonance experiments were investigated. The propagator formalism based on the loss of spin phase memory during random motion was applied to describe the diffusion-induced signal attenuation. The exact expression of the signal attenuation under the short gradient pulse approximation for restricted diffusion between two parallel plates was obtained using this propagator method. For long gradient pulses, a modified formalism was proposed. The simulated signal attenuation under the effects of gradient pulses of different width based on the Monte Carlo method agrees with the theoretical predictions. The propagator formalism and computer simulation can provide convenient, intuitive and precise methods for the study of the diffusion behaviors.

PACS: 82.56.Lz; 07.05.Tp

Keywords: Nuclear magnetic resonance; Restricted diffusion; Monte Carlo simulation; Inter-molecular multiple-quantum coherences

1. Introduction

Molecular self-diffusion is a random translation motion of molecules driven by the internal kinetic energy. Pulsed field gradient NMR has long been recognized as a useful means of probing migration of

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0921-4526/$ - see front matter
doi:10.1016/j.physb.2005.05.032

nuclear spins, inter-molecular interactions and self-aggregation [1–7]. The influence of boundary restrictions on fluid diffusivity has important implications for modeling of fluid transport in porous media [8]. It makes possible to extract information not only about the motion of molecules but also about the geometry of the boundaries and hence about the pore morphology of the surrounding medium [9]. The short gradient pulse (SGP) approximation has been successfully used to study restricted diffusion with SGPs during which diffusion of the molecules can be neglected. Since the SGP limit is not always physically realizable in practice, many efforts have been made to find convenient mathematical treatments that are applicable to the case of restricted diffusion in the presence of finite-width gradient pulses [10–12]. However, some obscured problems concerning measurements of diffusion in a system, for which restriction to motion causes a deviation from the Fickian behavior, remain open [13,14].

When a two-pulse NMR sequence separated by a time interval is applied to a highly polarized system, such as solid He^1, liquid He^2, and water, multiple spin echoes (MSEs) can be observed in the presence of magnetic field gradients [15–19]. The phenomenon has also been analyzed using the theory of inter-molecular multiple-quantum coherences (MQCs) [20]. Perhaps, the most important potential clinical application of inter-molecular MQCs arises from their sensitivity to sample structure at spatial dimensions around the dipolar correlation distance, which is determined by the area of the inter-molecular MQC-encode gradient pulse and is therefore under control of the experimenter. This specific sensitivity offers the possibility of assessing sample structure in vivo on a length scale far below the typical MRI pixel size [21]. The potential application of inter-molecular MQCs in MRI and in in vivo NMR related to diffusion has been studied [22]. Since intra- and inter-molecular MQCs represent different physical processes, their diffusion rates may be different. Our theoretical predictions, experimental observations and computer simulations have shown that the apparent diffusion rate of inter-molecular MQCs does not coincide with that of intra-molecular MQCs for free diffusion [23–25]. In this paper we developed a novel propagator formalism for describing NMR signal attenuation in the presence of molecular diffusion for inter-molecular MQCs. Using this propagator formalism and the Monte Carlo method, respectively, we studied the restricted diffusions of inter-molecular MQCs between two parallel plates. The propagator formalism was modified for the cases when the width of gradient pulse could not be ignored. The results of the propagator and Monte Carlo simulation are consistent and achieve high accuracy. These two methods are simple and intuitive, and suitable for studies of many special cases that are intractable with exact analytical solutions [26].

2. Theoretical considerations

2.1. Propagator formalism for traditional diffusion

In homo- and hetero-nuclear NMR experiments, it is convenient to describe the evolution of a selected coherence transfer pathway by the raising and lowering operators, I^+ and I^-. Under arbitrary gradient waveforms (time-dependent linear or nonlinear gradients), the raising and lowering spin operators evolve according to Sorensen et al. [27]:

$$I^{\pm} \xrightarrow{\int \gamma B(Z,t)\,\mathrm{d}t} I^{\pm} \exp\left[\mp \mathrm{i} \int \gamma B(Z,t)\,\mathrm{d}t\right], \tag{1}$$

where γ is the gyromagnetic ratio, Z is the position of spins in the z direction, and $B(Z,t)$ is the magnetic field intensity in position Z at time t. We first assume that the spin remains at the coordinate Z, without any random translation motion. Under the effect of the inhomogeneous magnetic field $B(Z,t')$ for a period t,