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Spin-diffusion approach for relaxation in bi-spaced periodic one-dimensional systems

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Abstract

A theoretical model for ^1H–^1H dipolar nuclear spin relaxation for a bi-spaced periodic one-dimensional array of spin 1/2 nuclei has been developed. A diffusion equation is formed for such a system by assuming nearest-neighbor interaction and isotropic random molecular reorientations. Under spin-diffusion conditions ($\omega\tau_c \gg 1$), this equation has been solved using Laplace transform for an infinite chain. The results are presented for the boundary conditions described for truncated driven Nuclear Overhauser effect experiments. The solution is further generalized by making the inter-spin spacing as a random variable with a Gaussian distribution.

Keywords: Spin diffusion; Nuclear Overhauser effect; Relaxation

1. Introduction

The transfer of magnetization from one spin to another via inter-nuclear dipolar interaction acting as a relaxation mechanism in liquids is known as Nuclear Overhauser effect (NOE). While the heteronuclear NOE is used to enhance the signal of nuclei with low gyro-magnetic ratio (γ), the proton–proton NOE's are used to study the solution structures of organic and bio-molecules [1–3]. The observed polarization of a spin, while saturating a nearby spin, can show an increase (positive NOE) or decrease (negative NOE) depending on the relative signs and magnitudes of γ of the two nuclei and the time scale of the motional processes of the molecules. The homonuclear NOE for organic and small bio-molecules which reorient rapidly such that $\omega\tau_c \ll 1$ (where ω is the Larmor frequency and τ_c is the correlation time of the isotropic random motion), is positive, weak, and does not migrate to many spins. On the other hand, for large bio-molecules, where $\omega\tau_c \gg 1$, NOE is negative, large in magnitude, and migrates over long distances within the molecule. This limit is therefore often referred as "spin-diffusion" limit [4–6].

It has been shown by Krishnan et al. [7,8] that in the spin-diffusion limit, the migration of spin magnetization in an one-dimensional chain can be described by a diffusion equation. The assumption of equidistant one-dimensional chain is well suited for systems such as helical peptides and proteins, which are deuterated at all positions except labile amide protons. In such cases, $d_{N,N+1}$, the distance between adjacent amide protons (denoted in literature as $d_{NN}(i,i+1)$), is short (~2.8 Å) [9] and shows pronounced sequential NOEs. However, in extended β sheet conformations of peptides and proteins in which the side chains are deuterated, the $NH_i - C^{\alpha}_{i-1}H$ distance (denoted as $d_{\alpha N}(i,i+1)$) is of the order of 2.2 Å, while the $NH_i - C^{\alpha}_{i}H$ distance ($d_{N\alpha}(i,i)$) is about 2.8 Å and the inter-spin distance is bi-spaced periodic as shown in Fig. 1 [9]. This continues throughout the chain. Similar distance pattern exist in other secondary structures for

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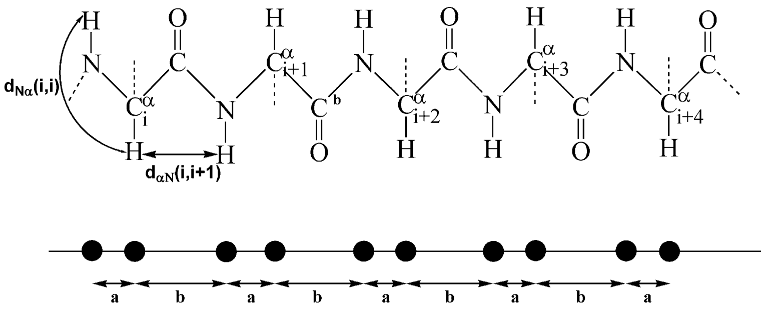

Fig. 1. Schematic diagram of short sequential ^{1}H–^{1}H connectivity in polypeptide segment of secondary structures. In extended β sheet conformation the $NH_i - C^{\alpha}_{i+1}H$ distance ($d_{\alpha N}$) is of the order of 2.2 Å, while the $NH_i - C^{\alpha}_{i}H$ distance ($d_{N\alpha}$) is about 2.8 Å [9].

example alpha helical $d_{\alpha N}(i, i+1) = 3.5$ Å, $d_{N\alpha}(i, i) = 2.2$ to 2.8 Å depending on Φ. 3_{10} helical chain $d_{\alpha N}(i, i+1) =$ 3.4 Å and $d_{N\alpha}(i, i) = 2.7$ Å [data from [9]]. Such a chain will be not linear but the migration of magnetization will be uni-directional (either forward or backward) and it can be considered as one-dimensional chain because all other leakage paths are blocked by the process of deuteration. Here, we are considering only intra-molecular NOE, ignoring inter-molecular NOEs. Also, in flexible polypeptide chains where most NOEs are quenched by motion, chain remains practically one-dimensional. In the present paper, we have therefore extended the one-dimensional equidistant model to bi-spaced periodic lattice model. The general rate equations for the spin populations have been formed and are solved for specific initial and boundary conditions for driven NOE experiment. For the future, we plan to extend current model to two- and three-dimensions to incorporate all NOE connectivities in protein conformations.

The distance measurement using NOE data and its modeling assumes fixed ^{1}H–^{1}H distances as taken by [7]. The real systems, such as proteins and nucleic acids in solution at ambient temperature, are not rigid. The interpretation of observed NOE for flexible system presents a difficult problem and needs to address theoretically [2]. In order to account for motional fluctuation of distance vector, the equidistance model of [7] is further extended for a one-dimensional stochastic chain having random inter-molecular distance with a Gaussian distribution.

It may be mentioned that Krishnan et al. [7] have shown that the migration of magnetization in a one-dimensional chain can be described by a second order diffusion equation only for driven NOE experiments in which the irradiated spin is assumed to be saturated for all times. It has been further shown by them that in experiments utilizing transient NOE, where the irradiated spin is selectively inverted at $t = 0$ and the migration of magnetization is monitored at other spins, higher order terms in the Taylor expansion are needed and the migration of magnetization can no longer be described by a second order “diffusion equation” [8]. In the following we therefore consider only the driven NOE experiment.

2. Spin-diffusion equation for bi-spaced lattice

A one-dimensional homo-nuclear chain of bi-spaced periodic lattice of spin 1/2 having dipolar coupling only is considered. It is assumed that each spin interacts with its nearest neighbor only. The spatial coordinates for these spins along one dimension have positions $\ldots x-2b-a, x-b-a, x-b, x, x+a, x+a+b, x+2a+b \ldots$ (Fig. 2). The population of the lower level of the spin at position x and time t is denoted by $n_+(x,t)$ and that of the upper level as $n_-(x,t)$ as shown in Fig. 2. The rate of change $n_+(x,t)$ can be written as

$$\begin{aligned}\frac{\partial n_+}{\partial t}(x,t) &= -n_+(x,t)W_{1a} - n_+(x,t)W_{1b} + n_-(x,t)W_{1a} + n_-(x,t)W_{1b}\\ &\quad - n_+(x,t)n_-(x+a,t)W_{0a} + n_-(x,t)n_+(x+a,t)W_{0a}\\ &\quad - n_+(x,t)n_-(x-b,t)W_{0b} + n_-(x,t)n_+(x-b,t)W_{0b}\\ &\quad - n_+(x,t)n_+(x+a,t)W_{2a} + n_-(x,t)n_-(x+a,t)W_{2a}\\ &\quad - n_+(x,t)n_+(x-b,t)W_{2b} + n_-(x,t)n_-(x-b,t)W_{2b}, \qquad (1)\end{aligned}$$

where W_{0r}, W_{1r}, and W_{2r} $(r = a, b)$ are, respectively, the zero, single, and double quantum transition probabilities with inter-spin spacing as r for a pair of spin 1/2 homonuclear spin system and are given by [10,11]:

$$\begin{aligned}W_{0r} &= \frac{1}{10}\frac{\gamma^4\hbar^2}{r^6}\tau_c,\\ W_{1r} &= \frac{3}{20}\frac{\gamma^4\hbar^2}{r^6}\left\{\frac{\tau_c}{1+\omega_x^2\tau_c^2}\right\},\\ W_{2r} &= \frac{3}{5}\frac{\gamma^4\hbar^2}{r^6}\left\{\frac{\tau_c}{1+4\omega_x^2\tau_c^2}\right\}, \qquad (2)\end{aligned}$$

with τ_c as the isotropic rotational correlation time. An expression similar to Eq. (1) can be written for $n_-(x,t)$. The magnetization would be proportional to $N(x,t) = [n_+(x,t) - n_-(x,t)]$. The rate of change of $N(x,t)$ is obtained as

$$\frac{\partial N(x,t)}{\partial t} = -2\rho N(x,t) - \sigma_a N(x+a,t) - \sigma_b N(x-b,t), \qquad (3)$$

where