

# Simulation of DNMR spectra using propagator formalism and Monte Carlo method

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## ABSTRACT

A new program—ProMoCS—is presented for the simulation of dynamic nuclear magnetic resonance spectra. Its algorithm is based on the Monte Carlo method as the one of the previously introduced MC-DNMR but the theory of ProMoCS is explained by using the statistical approach of propagator formalism. Our new program is suitable for the calculation of dynamic NMR spectra of spin systems up to 12 ½ spin nuclei, several conformers and any type of exchange between them. Mutual exchange of coupled spins can be simulated as well. While it keeps the main advantage of the Monte Carlo based method: calculation with significantly smaller matrices as compared with programs based on the simulation of the average density matrix, the maximum number of nuclei is increased significantly. Thus spectra of such systems can be simulated that was impossible previously.

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## 1. Introduction

Methods for the simulation of dynamic NMR spectra are well-known for systems with chemical exchange [1–7]. The most widespread simulation programs (DNMR5 [8–11], MEXICO [12–14], WinDNMR [15–16], Bruker's TOPSPIN DNMR module [17]) are based on the calculation of transitions using the average density matrix. The most important limitation of this method is the huge computer memory requirement even for simple spin systems. In the case of a spin system with  $n$  nuclei and  $s$  conformers the dimension of the coefficient matrix is proportional to  $s \cdot 4^n$ . This matrix blocks according to the coherence levels and these blocks are treated separately. The blocks with smaller sizes, the neglect of combinational transitions and the use of sparse matrix diagonalization methods [18–19] can reduce the computer memory requirement radically, but the reduced matrix still can be too big for more complicated spin systems.

Our MC-DNMR program based on the theory of Monte Carlo simulations was introduced as alternative simulation algorithm with less memory requirement previously [20]. The theory of that program was based on the extension of single spin vector model to coupled spin systems, by which the chemical exchange could be incorporated into the vector model. The memory requirement of this program is significantly smaller than that of the programs mentioned above. However, in cases of scalar coupling between the exchanging sites the simulated high temperature spectrum yields in non-realistic multiplets.

In order to correct this error the theoretical background of the Monte Carlo simulations of DNMR spectra is now presented using the propagation of individual density matrices. A new program called ProMoCS (Propagation & Monte Carlo Simulation) was written which gives correct results even in cases where MC-DNMR fails.

## 2. Theoretical background

The well-known method for the simulation of dynamic NMR spectra is based on the solution of Liouville–von Neumann equation [21]:

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

As a first step this equation is converted into the Liouville space. This means that the average density matrix ( $\bar{\rho}$ , function of  $t$  time) becomes a vector ( $\bar{\sigma}$ ) and its commutator with the Hamiltonian ( $H$ ) transform to a superoperator ( $\bar{L}$ ):

$$\frac{d\bar{\sigma}}{dt} = -i\bar{L}\bar{\sigma}. \quad (2)$$

In order to describe the relaxation and dynamic processes two additional terms are included: the Redfield-type relaxation ( $R$ ) and the exchange ( $X$ ) matrices, resulting in:

$$\frac{d\bar{\sigma}}{dt} = -(i\bar{L} + R + X)\bar{\sigma}. \quad (3)$$

The solution of this equation gives the evolution of the density matrix as a function of the time elapsed as:

$$\bar{\sigma}(t) = \exp(-(i\bar{L} + R + X)t)\bar{\sigma}_0, \quad (4)$$

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where  $\bar{\sigma}_0$  is the density matrix at the start of detection ( $t = 0$ ). From now the relaxation is approximated with the multiplication of the time domain signal with an exponential at the end of the calculation so the matrix  $R$  can be neglected in Eq. (4). The signal (*fid*) is then calculated as the scalar product of the density matrix and the vector of the  $I^+$  operator:

$$fid(t) = \langle I^+ | \bar{\sigma}(t) \rangle. \quad (5)$$

The *average* density matrix calculated by this method describes the average of molecular states in the whole system. This means that all sites are included in it (Fig. 1a). Spins are distinguished by their chemical environment (and chemical shift) and not by the individual nucleus they belong to. The coefficients in the density matrix represent the populations of the coherences.

For our purposes we define the *individual* density matrix ( $\rho$  or  $\sigma$ ). This matrix describes the probabilities of the possible spin states of the nuclei in one individual molecule. From now we use the name *spin set* for these nuclei. In an exchanging system a given spin set can change its chemical environment but the nuclei remain together in it. In different chemical environments the density matrix evaluates differently (e.g. the Hamiltonian depends on the chemical environment). As molecules can convert into each other at any time, the chemical environments, Hamiltonians and propagators of spin sets are permuted randomly in time.

The *fid* of a spin set can be calculated from its own density matrix as it is shown later. The sum of the *fids* of a few hundreds or thousands of randomly selected spin sets gives the overall *fid* which is a good approximation of the macroscopic signal (Monte Carlo method).

In order to construct the algorithm of the simulation the followings should be given: the method for the determination of the lifetimes of the conformers and the mathematical forms of the operators of precession, detection and exchange.

The time of an exchange (to be called exchange points and noted as  $t_r$ ) is determined statistically based on the rate coefficients of the exchanges. The lengths of intervals between two exchange points (time slices) have exponential distribution with the average lifetime ( $\tau_i$ ) of the molecule as its parameter [20]:

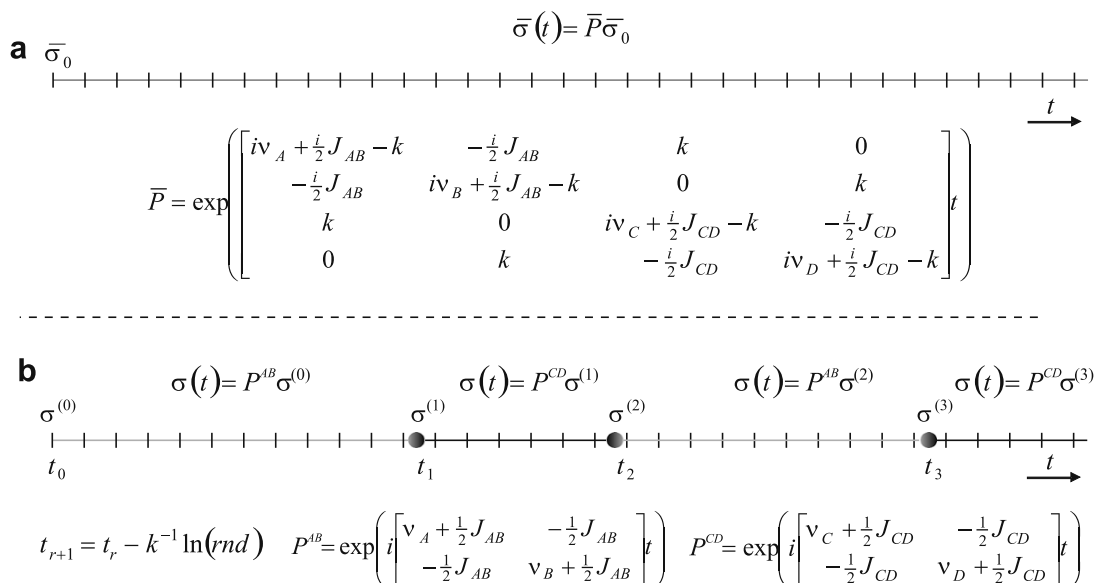
$$t_{r+1} - t_r = -\tau_i \ln(rnd) = -\left(\sum_j k_{ij}\right)^{-1} \ln(rnd), \quad (6)$$

where *rnd* is a random number and  $k_{ij}$  is the rate coefficient of the exchange from molecule  $i$  to  $j$ .

During an exchange, which is assumed to happen in negligible time (instant jump approximation), the spin set remains unaltered, only the chemical environment and its parameters like chemical shift and coupling constants of the corresponding nucleus alter. This affects only the precession operator but not the density matrix (Fig. 1b). As a consequence the precession operator of the  $r$ -th time slice has to be replaced by a new one according to the new state in time slice  $r + 1$  at the beginning of the ( $r + 1$ )th time slice (e.g. replace  $P^{AB}$  with  $P^{CD}$  at  $t_1$  for  $r = 1$  on Fig. 1b). After the exchange the simulation for time slice  $r + 1$  is continued using  $\sigma^{(r)}$  (the density matrix at  $t_r$ ).

The *fid* of the  $r$ -th time slice for one molecule is calculated at the detection points that fall into the corresponding interval. If the rates of exchanges are so fast, that there are more than one exchange points between two sampling points, there must be time slices without sampling point. In the case of such 'dummy' slices only the density matrix is propagated to the end of this time slice. The *fid* of the spin set (scan) is the union of the *fids* of the time slices and the spectrum of the whole system is calculated as the Fourier transform of the sum of the scans. This method is described in detail in Ref. [20].

As the exchange is handled as a propagating effect of the density matrix, the whole exchanging spin system (including the spins of all conformers) can be simulated by calculating with only one static (only  $J$ -coupled) spin set. Therefore the basis set used for the simulation is made of the basis functions of one spin set. The size of basis set is  $\sim 2^n$  where  $n$  is the number of nuclei in the spin set. In fact the Hamiltonian, the density matrix and the precession operator blocks according to the coherence levels and the size of the largest block is only  $\binom{n}{n/2}$ . This size still means an exponentially scaling memory requirement but is significantly smaller than the memory needed for the conventional calculations [8–17] using density matrix blocks. The RAM requirement of the program is independent of the number of exchanging sites.



**Fig. 1.** Propagation of the (a) average (b) individual density matrix. Ticks show the points of detection (where *fid* points are calculated) and dots show the points of exchange. As an example, the propagators ( $\bar{P}$  and  $P^{AB}$ ,  $P^{CD}$ ) of an exchanging  $AB \leftrightarrow CD$  spin system are shown for both calculations.

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